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INVESTIGATION OF POLYMERIZATION AND PROPERTIES OF MIXED POLYESTERS OF THE ACRYLIC SERIES

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We previously reported the synthesis of a new group of derivatives of the acrylic series, namely polyester acrylates [1].

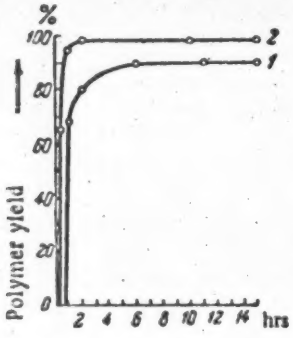
In the present communication an examination is made of the connection between the structure of the polyester acrylates, their capacity for three-dimensional polymerization and the physicomechanical properties of the polymers.

The subjects for the investigation were (bis-ethylene glycol) - phthalate dimethacrylate, (bis-diethylene glycol) - phthalate dimenthacrylate, (bis-triethylene glycol) - phthalate dimethacrylate, (bis-triethylene glycol) - sebacate dimethacrylate, (bis-glycerol) - phthalate tetramethacrylate and (bis-glycerol) - sebacate tetramethacrylate.

The substances indicated differed in the nature and the elasticity of the groups forming the cross links of the steric structure of the polymer and also in the number of reactive double bonds.

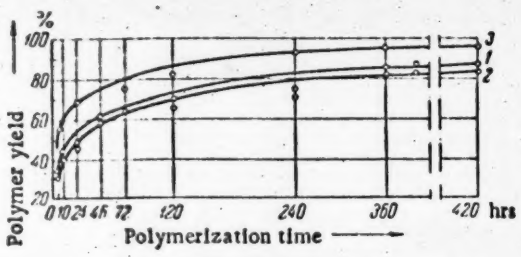
Block polymerization was carried out at temperatures of 65 and 20 – 25° in the presence of benzoyl peroxide.

A study of the polymerization kinetics established that in all cases the polymerization of tetra- and octafunctional polyester acrylates proceeded with an induction period, during which the viscosity and refractive index did not change.



Time of polymerization

Fig. 1



rig. 2

During the subsequent period there occurred instantaneous gelling of the whole monomer mass with complete loss of fluidity and conversion into insoluble three-dimensional polymers.

TABLE 1

Physicomechanical Properties of Polymers•

Exp. No.	Polymer	Specific resilience, kg/cm.cm²	Brinell hardness, kg/mm²
1	Poly-(triethylene glycol dimethacrylate)	2.0	10.9
2	Poly-[(bis-ethylene glycol)-phthalate dimethacrylate]	6.0	24.0
3	Poly-[(bis-diethylene glycol)-phthalate dimethacrylate]	10.8	26.7
4	Poly-[(bis-triethylene glycol)-phthalate methacrylate]	19.3	30.5
5	Poly-[(bis-triethylene glycol)-sebacate methacrylate]	25.5	40

• The infusible, insoluble polymers withstood heating to 220 – 260°.

To elucidate the effect of molecular functionality of the polyester acrylates on their capacity for three-dimensional polymerization, we compared the rates of polymerization of octafunctional (bis-glycerol)-phthalate tetramethacrylate (Fig. 1, 1) and tetrafunctional (bis-triethylene glycol)-phthalate dimethacrylate (Fig. 1, 2). As is seen, with an increase in the number of double bonds, the rate of polymerization of the esters increased sharply.

In contrast to tetrafunctional polyester acrylates, in the presence of benzoyl peroxide octafunctional polyester acrylates ((bis-glycerol)-phthalate and -sebacate tetramethacrylates) were capable of forming glass-like polymers at 20 – 25° (Fig. 2).

An examination of the curves in Fig. 2 shows that in the polymerization of octafunctional polyester acrylates at a temperature of 20 – 25° in the presence of 1% benzoyl peroxide, 70% of insoluble polymer was formed after five days. Further polymerization proceeded more slowly. The yield of insoluble polymer reached 82 – 85% only after 15 days.

A comparison of curves 1 and 2 in Fig. 2 shows that the rate of polymerization of different esters with the same functionality depended on the distance of the reactive groups from each other.

Thus, (bis-glycerol)-sebacate tetramethacrylate (curve 2) polymerized more slowly than (bis-glycerol)--phthalate tetramethacrylate (curve 1) and this may be explained by steric effects of the radical between the double bonds of the monomer.

During the work it was established that atmospheric oxygen inhibited the polymerization of polyester acrylates and the introduction of a siccative (siccative 7640 – a 35.5% white alcohol solution of a melt of cobalt resinate with a drying oil and lead-manganese linoleate) eliminated this phenomenon. As Fig. 2 shows, the introduction of a siccative increased the polymerization rate of octafunctional esters at a temperature of 20 – 25° (curve 3).

The yield of insoluble polymer reached 85% after five days and 92% after 10 days. Extending the time to 20 days led to only a 3% increase in the polymer yield.

A difference in the structures of polyfunctional mixed esters of methacrylic acid undoubtedly must be reflected in the magnitude of the volume contractions during polymerization and in the physicomechanical properties of the polymers.

An investigation of the kinetics of contraction phenomena during polymerization of polyester acrylates showed:

1. Among the tetrafunctional esters, with an increase in the separation between the functional groups the volume contractions decreased. Thus, (bis-ethylene glycol)-phthalate dimethacrylate had a contraction

equal to 5.4%, while (bis-triethylene glycol)-sebacate dimethacrylate had one of 1.6%. This indicates that with an increase in the separation between the double bonds of the monomer, polymers with more loosely packed macromolecules are formed [2].

2. Among the octafunctional polyester acrylates, a change in the separation between the pairs of double bonds has hardly any effect on volume contractions during polymerization. Thus, (bis-glycerol)-phthalate tetramethacrylate and (bis-glycerol)-sebacate tetramethacrylate have equal contractions (0.5%).

This fact is in full agreement with ideas on the effect of the nature and elasticity of "cross-linking groups" on volume contraction during three-dimensional polymerization.

Actually, removal of glycerol dimethacrylate groups from the molecule of the octafunctional polyester acrylates investigated does not change the separation between neighboring pairs of chains and, consequently, has hardly any effect on the volume changes in the first stage of three-dimensional polymerization of the monomer.

The effect of the structure of the polyfunctional esters of methacrylic acid on the physicomechanical properties of the polymeric products were characterized by the values of specific resilience and hardness. Data from physicomechanical tests of the polymer properties are presented in Table 1.

As can be seen, the specific resilience and hardness of the infusible, glass-like polymers increases with a decrease in the density of packing of the cross-linked chains of the macromolecules (Exps. No. 1 – 4) and with an increase in the flexibility of the cross-linking groups (Exps. Nos. 4 and 5).

The increase in hardness with the increase in size and elasticity of the cross-links is apparently due to the decrease in internal strain, usually produced as a result of contractions during transition from monomer to polymer.

Thus, polyester acrylates offer the possibility of obtaining polymers with a minimal volume change, coupled with high thermal stability, hardness and resilience.

In this connection, polymers of polyester acrylates have considerable advantages over known types of infusible polymeric products and this offers us wide prospects of applying them as binding and reinforcing plastics, casting materials, compounds, components of adhesives and lacquer compositions, special pastes and other types of polymeric materials.

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REDUCTIVE ACETYLATION OF NITRO COMPOUNDS OF THE THIOPHENE SERIES IN THE PRESENCE OF RANEY NICKEL

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We showed previously [1] that the action of Raney nickel (Ni_R) on 5-nitro -2-thiophenecarboxylic acid I formed δ-aminovaleric acid. The yield of the latter, however, was very small. Starting from the observation that the hydrogenolysis of acetylamino acids of the thiophene series proceeds in better yield than hydrogenolysis of the corresponding amino acids [2], we attempted to increase the yield by using acetic anhydride as the reaction medium. Under these conditions, the intermediate product, 5-amino-2-thiophenecarboxylic acid, could have formed the more stable 5-acetylamino-2-thiophenecarboxylic acid II, which should have improved the yield of the aliphatic acetylamino acid (III):

I II III

However, we were able to isolate only acetylamino acid II from the mixture formed during the reaction. Since this compound forms (III) under the action of Ni_R in an aqueous medium [3], from the data of our experiment it follows that acetic anhydride deactivates Ni_R as a desulfurizing agent. This conclusion was also confirmed on other examples: when heated with Ni_R in acetic anhydride 2-nitrothiophene and 4-nitro-2-thiophenecarboxylic acid also formed the corresponding acetylamino compounds and 3, 5-dinitro-2-methylthiophene was reduced to the acetylamino nitro derivative. Thus, under the given conditions the reaction of Ni_R with nitro derivatives of thiophene stops at the stage of formation of the acetylamino compound or, in other words, the process leads to reductive acetylation.

The effect of solvent on the reducing properties of Ni_R in the hydrogenolysis of thiophene derivatives was noted previously [4], but we were unable to find any mention in the literature of the capacity of acetic anhydride for suppressing the desulfurizing function of Ni_R in its action on nitro derivatives of thiophene. In connection with this we will point out that our attempt to obtain acetylamino acid II by the method proposed for the reductive acetylation of certain nitro compounds [5], namely by the action of zinc in a medium of acetic acid and anhydride, was unsuccessful since the product formed a tar.

In identifying 5-acetylamino-2-thiophenecarboxylic acid II we encountered the fact that data on its properties presented in the literature are contradictory. Hartough [6], referring to the work of Steinkopf and Muller [7], reported m.p. 272 – 273° for it, although the latter authors gave this constant for 4-acetylamino-2-thiophenecarboxylic acid. Campaigne and Archer [8] described the preparation of acetylamino acid II by the oxidation of 5-acetylamino-2-thiophenealdehyde (IV) and also reported m.p. 271 – 272° for it and thus confirmed the figure mistakenly reported by Hartough. This discrepancy first attracted the attention of Cymerman-Craig and Willis [9], though they later [10] arrived at the conclusion that Steinkopf actually had acetylamino acid II and not the isomeric 4-acetylamino-2-thiophenecarboxylic acid. Finally, in 1957 Tirouflet and Chane [11] reported the preparation of II with m.p. 272° by hydrolysis of its methyl ester.

Since the m.p. (230 – 232°) of the acetylamino acid we obtained, to which we ascribed structure II in accordance with the method of its formation, did not agree with that indicated above (272°), it was necessary to confirm the position of the acetylamino group in the ring. With this purpose, the acetylamino acid with m.p. 230 – 232° was heated in vacuum; here decarboxylation gave a good yield of 2-acetylaminothiophene with m.p. 160 – 160.5°; the isomeric 3-acetylaminothiophene [12] has m.p. 147 – 148°. Further confirmation for structure II for the substance with m.p. 230 – 232° was found in the facts that the methyl and ethyl esters obtained from it had m.p. 171.5 and 161 – 162°, which correspond exactly with literature data [11, 13] and differ sharply from the constants of the esters of 4-acetylamino-2-thiophenecarboxylic acid we obtained (135 –136° and 116 –117°). A very significant result is the fact that hydrogenolysis of the acetylamino acid II (m.p. 230 – 232) and subsequent heating of the product with hydrochloric acid gave the hydrochloride of δ-aminovaleric acid, from which we obtained δ-benzoylaminovaleric acid.

In the light of these data, we were doubtful about the reliability of the experimental data of Campaigne and Archer [8] (see above). The actual possibility of oxidizing aldehyde IV to acid II with Fehling's solution seemed improbable since there is a report in the literature [14] that aromatic aldehydes are not oxidized by this reagent. Nonetheless, we considered it necessary to attempt to carry out Campaigne and Archer's experiment. When aldehyde IV was kept with Fehling's solution, a precipitate of cuprous oxide actually appeared. When the precipitate had been removed, the filtrate was made acid with hydrochloric acid.• This precipitated a substance with m.p. 273 – 274° (corr.), which had a neutralization equivalent (n.e.) of 188. In its properties it was almost identical with the oxidation product described by Campaigne and Archer (m.p. 271 – 272°, n.e. 182) and similar in n.e. value to acetylamino acid II (n.e. 185). However, this substance did not contain N or S and, as was found later, was acid potassium tartrate (m.p. 273 –274°, n.e. 188.2). One gets the impression that due to an unusual coincidence of circumstances (agreement of melting points and similarity of n.e.), Campaigne and Archer accepted this acid salt as the acetylamino acid.••

Our attempts to oxidize aldehyde IV to acid II with silver oxide and also $KMnO_4$ in pyridine were unsuccessful: in both cases an uncrystallizable, colored substance was obtained.

EXPERIMENTAL

5-Acetylamino-2-thiophenecarboxylic acid II. To a stirred solution of 7.0 g of nitro acid I (m.p. 157 – 158°, obtained from 2-iodothiophene [13]) in 175 ml of acetic anhydride, heated to 40°, was added about 30 g of freshly prepared Ni_R. The temperature then rose to 85°. The mixture was cooled to 60° and stirred for a further 1.5 hours at 65 – 70°. The warm solution was filtered free from Ni and the precipitate washed with hot acetic anhydride and acetone. The combined filtrates were evaporated to dryness in vacuum, the residue dissolved in dilute alkali and the solution filtered and acidified with hydrochloric acid. The precipitated crystals were collected, washed with water and dried. The weight was 4.6 g (61.3% yield). After recrystallization from water, the substance had m.p. 230 –232° (decomp.).•••

The average yield (from 6 experiments) was 47% of theoretical.

Found %: C 45.63; 45.46; H 4.01; 3.85; N 7.27; 7.22; S 17.32; 17.34. $C_7H_7O_3NS$. Calculated %: C 45.39; H 3.81; N 7.56; S 17.31.

An attempt to obtain the hydrochloride of 5-amino-2-thiophenecarboxylic acid by hydrolysis of the acetylamino group by heating II with hydrochloric acid was unsuccessful; an attempt to hydrolyze the acetylamino acid by heating with barium hydroxide solution was also without result.

Methyl ester of acetylamino acid II. To a suspension of 3.0 g of acetylamino acid II in 100 ml of ether was gradually added an ether solution of 2.3 g of diazomethane. The evolution of nitrogen proceeded slowly. The mixture was left overnight. The solvent was removed. The residue was 3.3 g of a substance with m.p. 165 –168°. After recrystallization from dilute alcohol, the substance had m.p. 171 –171.5° (corr.). Literature data [11]: m.p. 172°.

•No mention is made of acidification in the work of Campaigne and Archer, but without this operation it would be impossible to precipitate the acetylamino acid from a solution with an alkaline reaction to phenolphthalein.

••Elementary analysis data for the substance with m.p. 272 – 273° is not given in paper [8].

•••The m.p. depended on the heating rate.

Found %: C 47.92; 48.13; H 4.63; 4.56; N 7.03; 7.07; S 15.93; 15.76. $C_8H_9O_3NS$. Calculated %: C 48.22; H 4.55; N 7.03; S 16.10.

The ethyl ester of acetylamino acid II was obtained by the action of a solution of diazoethane on acetylamino acid II; after recrystallization from dilute alcohol, the substance had m.p. 161 – 162° (corr.). Literature data [13]: m.p. 160 – 162°.

Found %: C 50.57; 50.68; H 5.10; 5.08; N 6.75; 6.62; S 14.87; 14.88. $C_9H_{11}O_3NS$. Calculated %: C 50.69; H 5.20; N 6.57; S 15.04.

Hydrogenolysis of acetylamino acid II. To a stirred solution of 3.15 g of II in 100 ml of water and 30 ml of concentrated ammonia solution at 60° was added about 18 g of Ni_R, stored under water. Stirring at 65 – 70° was continued for 3 hours. The Ni was removed by filtration and washed with warm water. The filtrates were evaporated in vacuum. The residue (2.6 g) crystallized on standing and had m.p. 72 – 73°. The substance obtained was dissolved in 50 ml of dilute (1 : 1) HCl, the solution boiled for 3 hours and the HCl then removed in vacuum. After reprecipitation with ether from an isopropyl alcohol solution, the hydrochloride formed had m.p. 85 – 87°. Literature data [15] for the hydrochloride of δ-aminovaleric acid: m.p. 84 – 86°. The hydrochloride was treated with benzoyl chloride in the presence of NaOH and $NaHCO_3$ to give δ-benzoylaminovaleric acid with m.p. 103 – 106°. Literature data [16]: m.p. 106 – 107°.

Found %: C 65.19; 65.03; H 6.98; 6.91. $C_{12}H_{15}O_3N$. Calculated %: C 65.14; H 6.83.

Decarboxylation of acetylamino acid II. 1.0 g of II was melted at normal pressure in an apparatus for vacuum sublimation (bath temperature 230°) and the melt kept for 5 minutes at the m.p. and then sublimed at a bath temperature of 125 –130° and a pressure of 4 mm. We obtained 0.6 g (80% yield) of 2-acetylaminothiophene with m.p. 158.5 – 159.5° (corr.). After recrystallization from $CHCl_3$, the substance had m.p. 160 – 160.5° (corr.). A mixture of this substance with a sample of 2-acetylaminothiophene (m.p. 161 – 162°), obtained by a known method [17], melted at the same temperature.

Found %: C 51.07; 50.95; H 5.03; 4.98; N 9.72; 9.69; S 22.78; 22.71. C_6H_7ONS. Calculated %: C 51.04; H 5.00; N 9.92; S 22.71.

4-Acetylamino-2-thiophenecarboxylic acid. By reductive acetylation of 9.0 g of 4-nitro-2-thiophenecarboxylic acid [18] at 65 – 70° with a stirring time of 14 hours, we obtained 0.96 g (10% yield) of 4-acetylamino-2-thiophenecarboxylic acid, which had m.p. 273 –274° (decomp.) after recrystallization from dilute alcohol (with charcoal). Literature data [7]: m.p. 272 –273°.

Found %: C 45.17; 45.37; H 3.74; 3.96; N 7.12; 7.25; S 17.00; 17.19. $C_7H_7O_3NS$. Calculated %: C 45.39; H 3.81; N 7.56; S 17.31.

The methyl ester of 4-acetylamino-2-thiophenecarboxylic acid was obtained by the action of diazomethane on 4-acetylamino-2-thiophenecarboxylic acid. The m.p. was 135 – 136° (corr.), after recrystallization of the substance from water.

Found %: C 48.22; 47.98; H 4.58; 4.56; S 15.86; 15.90. $C_8H_9O_3NS$. Calculated %: C 48.22; H 4.55; S 16.10.

The ethyl ester of 4-acetylamino-2-thiophenecarboxylic acid was obtained by the action of diazoethane on the acetylamino acid; the m.p. was 116 – 117° (from water and from a mixture of n-hexane and benzene)).

Found %: C 50.66; 50.71; H 5.27; 5.24; S 14.97; 14.92. $C_9H_{11}O_3NS$. Calculated %: C 50.69; H 5.20; S 15.04.

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STUDY OF THE ELECTROCHEMICAL CONDENSATION OF THE MONO-2-ETHYLHEXYL ESTER OF ADIPIC ACID

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The electrochemical condensation of monoesters of dicarboxylic acids is of considerable practical and theoretical interest in connection with the increasing demand for high-molecular dicarboxylic acids and their esters. This process proceeds at the anode in the electrolysis of a solution of the monoester salt in nonaqueous or aqueous electrolytes [1]. In the present work a method was obtained for the first time for the electrosynthesis of the di-2-ethylhexyl ester of sebacic acid, which can be used as the basic component of high-grade lubricating materials [2].

The nonaqueous electrolytes used previously for the preparation of dimethyl sebacate [3, 4] are inconvient for practical use of electrochemical condensation due to the difficulty of isolating the diester from the electrolyte. In addition, as we were able to establish, methanol or ethanol cannot be used as the reaction medium for the preparation of di-2-ethylhexyl sebacate due to a transesterification reaction. In this case the electrolysis products are mixed diesters. Previously published data on the use of aqueous electrolytes for the preparation of diethyl sebacate give a low yield of electrosynthesis products [1].

In this investigation, the electrosynthesis of di-2-ethylhexyl sebacate was accomplished in an aqueous solution of the following composition: 300 — 400 g/liter of mono-2-ethylhexyl adipate, 30 -- 50 g/liter K_2CO_3 and 600 — 700 ml of water. The anode and cathode were platinum. No diaphragm was used. The electrolyte temperature was 20 — 30°. The current density at the anode was varied over a wide range from 10 to 60 amp/dm^2 and it was shown that over this range the yield of the main product, di-2-ethylhexyl sebacate, did not change and that the current density only affected the ratio of the electrolysis side products. For complete treatment of the monoester in the solution, it was necessary to pass 1.3 times the theoretical amount of electricity. The yield of di-2-ethylhexyl sebacate was 55% of theoretical.

A peculiarity of the electrolysis of mono-2-ethylhexyl adipate is strong foam formation, leading to loss of electrolyte. To eliminate foam formation we used the method of isolating extraction. Diethyl ether was used as the extractant and a layer of this above the electrolyte extracted the neutral electrolysis products.

The following processes may occur at the anode in the electrolysis of an aqueous solution of the adipic acid monoester:

$$OH^- - e \rightarrow OH_{ads} \qquad (1)$$

$$ROOC(CH_2)_4COO^- - e \rightarrow ROOC(CH_2)_4COO^{\cdot}, \qquad (2)$$

where R is $CH_3CH(C_2H_5)CH_2(CH_2)_2CH_2$.

The radical $ROOC(CH_2)_4COO$ is probably converted into a more energetically stable state by the elimination of CO_2:

$$ROOC(CH_2)_4COO^{\cdot} \rightarrow ROOC(CH_2)_4^{\cdot} + CO_2. \qquad (3)$$

At very high anode potentials, attained at a platinum electrode at considerable current densities, there occurs over-excitation of the radical ROOC $(CH_2)_4$ as a result of which the following reaction is possible:

$$ROOC(CH_2)_4^{\cdot} + {}^{\cdot}(CH_2)_4COOR \rightarrow ROOC(CH_2)_3CH^{=} + ROOC(CH_2)_3CH_3. \quad (4)$$

It is possible that in certain cases, reaction (5) may be a source of biradicals.

$$ROOC(CH_2)_4^{\cdot} + OH_{ads} \rightarrow ROOC(CH_2)_3CH^{=} + H_2O. \quad (5)$$

All the compounds detected and identified in the present work are the products of interactions between the radicals formed in reactions 1, 3, 4 and 5.

The fraction boiling in the range 90 – 220°/ 2mm, in addition to 2-ethylhexylvalerate formed by reaction 4, contained the 2-ethylhexyl esters of the monobasic acids, hydroxyvaleric and pentenoic, formed respectively in the reactions

$$ROOC(CH_2)_4^{\cdot} + OH_{ads} \rightarrow ROOC(CH_2)_4OH, \quad (6)$$

$$ROOC(CH_2)_3CH^{=} \rightarrow ROOC(CH_2)_2CH = CH_2.$$

The medium fractions, boiling in the range 250 – 260°/ 2 mm Hg, contained di-2-ethylhexyl sebacate, formed by reaction (8):

$$2ROOC(CH_2)_4^{\cdot} \rightarrow ROOC(CH_2)_8COOR, \quad (7)$$

and also di-2-ethylhexyl 4-octene-1, 8-dicarboxylate

$$2ROOC(CH_2)_3CH^{=} \rightarrow ROOC(CH_2)_3CH = CH(CH_2)_3COOR. \quad (8)$$

In the vacuum distillation residue (above 260°/ 2 mm Hg) was detected a compound formed as a result of a reaction in which all three radical participated:

$$2ROOC(CH_2)_4^{\cdot} + {}^{=}CH(CH_2)_3COOR \rightarrow ROOC(CH_2)_3CH\begin{matrix}(CH_2)_4COOR\\(CH_2)_4COOR\end{matrix} \quad (9)$$

A mixture of the tri-2-ethylhexyl ester of 5-propyl-5''' -carboxynonane-1, 9-dicarboxylic acid obtained with di-2-ethylhexyl sebacate should improve its viscosity characteristics and thermooxidative stability.

It is characteristic that we could not detect among the electrolysis products compounds which could have been formed by interaction of the radicals OH_{ads} and ROOC $(CH_2)_4COO^{\cdot}$, i.e., H_2O_2, ROOC $(CH_2)_4$ COOOH and ROOC $(CH_2)_4$ COO – OOC $(CH_2)_4$ COOR. From this it follows that the hydrogen peroxide theory of Kolbe's electrosynthesis, recently developed by Glasstone [5], is not justified in this case. Similar conclusions were drawn on the basis of the electron-radical theory by Sugino [6] with regard to the scheme of Kolbe's electrosynthesis.

However, while there is some similarity to Kolbe's electrosynthesis, the electrochemical condensation of monoesters of dicarboxylic acids is a more complicated process and one cannot completely extend to it the same rules that were established for the simplest case of the electrolysis of monobasic carboxylic acids.

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A NEW ORDER OF POLYMORPHIC CONVERSIONS OF Na_2BeF_4

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Sodium fluoroberyllate (Na_2BeF_4) was first obtained by Marignac [1] from aqueous solution. He observed two crystalline forms of Na_2BeF_4 which sometimes crystallized from solution together. The crystals of one form were found to be rhombic bipyramidal and of the the other form, monoclinic-prismatic.

The rhombic modification of Na_2BeF_4 was investigated by x-ray methods by G. S. Zhdanov and N. G. Sevast'yanov [2] and then by O'Daniel and Tscheischwili [3]. The authors of paper [3] found that the rhombic modification of Na_2BeF_4 belongs to the same structural type as silicates of the olivine group Ca_2SiO_4, Mg_2SiO_4, $CaMgSiO_4$, etc.

In the work of Thilo [4, 5, 6] and then Roy and Osborn [7] and Toropov [8] it was established that all the polymorphic forms of Na_2BeF_4, formed by heating the rhombic modification of Na_2BeF_4 and isolated from the melt, were also structural analogs of the Ca_2SiO_4 modification. Together with the rhombic modification, evaporation of an aqueous solution of Na_2BeF_4 frequently deposited crystals in the form of small needles.

X-ray pictures of the powdered needles crystals and of the rhombic ones were identical and evidently as a result, in papers [6] and [8] the needle-like crystals were taken as a γ-modification of Na_2BeF_4 and in addition, as we had shown, the period along the axis of the needles is very close to one of the parameters of the γ-modification.

In the present work we made thermographic and x-ray investigations of the needle-like crystals of Na_2BeF_4 obtained from aqueous solution, and found that they were a new and independent modification of Na_2BeF_4 to which we will subsequently refer as δ-Na_2BeF_4.

Investigation of δ-Na_2BeF_4. Needle-like crystals of Na_2BeF_4 were obtained by evaporating a solution of Na_2BeF_4, to which 2 — 3 drops of 40% hydrofluoric acid had been added per 50 ml of solution, in a platinum dish in a desiccator over sulfuric acid. Sometimes, together with the needle form, crystallization of the rhombic γ-form of Na_2BeF_4 also was observed.

The needle crystals were separated from the rhombic ones with a platinum wire under a microscope, transferred to a filter paper and dried for several days in a desiccator over sulfuric acid.

Found %: Na 35.07; 35.01 Be 6.67. Na_2BeF_4. Calculated %: Na 35.09; Be 6.86

The sodium content was determined through sodium zinc uranyl acetate [9] and the beryllium in the form of BeO [10].

The specific gravity of δ-Na_2BeF_4, determined in xylene, was found to be $d_4^{18} = 2.406 \pm 0.002$. The specific gravity of the rhombic form of Na_2BeF_4, $d_4^{20} = 2.455$ (2).

• The x-ray investigation were carried out by Yu. P. Simanov and L. M. Kovba.

The heating thermogram presented in Fig. 2 shows that when γ-Na_2BeF_4 is investigated, conversions occur at the following temperatures:*

$$\gamma\text{-}Na_2BeF_4 \xrightarrow{220^\circ} \alpha'\text{-}Na_2BeF_4 \xrightarrow{326^\circ} \alpha\text{-}Na_2BeF_4 \xrightarrow{600^\circ} \text{melt.}$$

Fig. 3 illustrates the heating thermogram of the δ-form of Na_2BeF_4. In the case the conversions occur at the following temperatures:

$$\delta\text{-}Na_2BeF_4 \xrightarrow{405^\circ} \varepsilon\text{-}Na_2BeF_4 \xrightarrow{435^\circ} \eta\text{-}Na_2BeF_4 \xrightarrow{500^\circ}$$
$$\leftarrow \theta\text{-}Na_2BeF_4 \xrightarrow{545^\circ} \varkappa\text{-}Na_2BeF_4 \xrightarrow{580^\circ} \text{melt.}$$

This series evidently corresponds to monotropic conversions since there are no thermal effects on cooling thermograms of preparations heated to 560° and thermograms of repeated heating show only the effect of fusion of Na_2BeF_4. Sometimes an effect was detected at 500° during a second heating. The melting point of Na_2BeF_4 depends on the

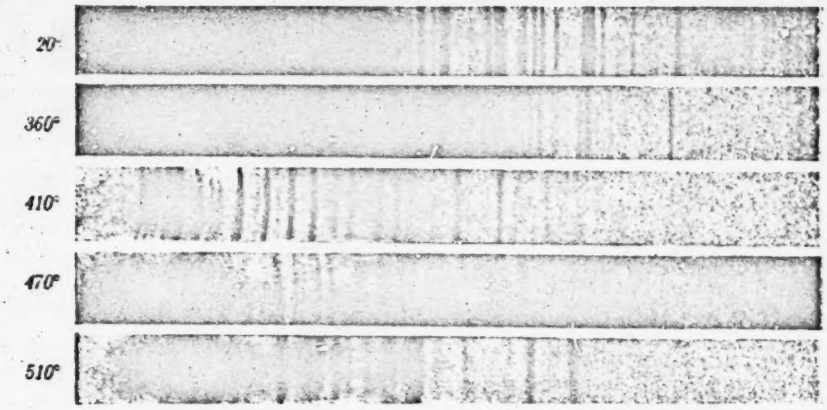

Fig. 1. X-ray pictures of δ-Na_2BeF_4 at various temperatures

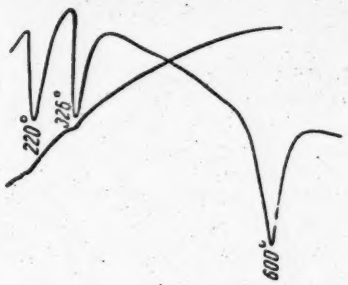

Fig. 2. Heating thermogram of γ-Na_2BeF_4

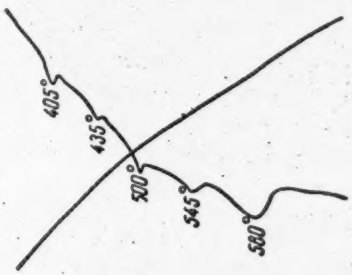

Fig. 3. Thermogram of δ-Na_2BeF_4

* For the polymorphic forms of Na_2BeF_4 Thilo [4] introduced designations analogous to the designations of the polymorphic forms of Ca_2SiO_4.

TABLE 1

Comparison of Results of X-ray Investigation of Conversions of δ-Na_2BeF_4 with Conversions of γ-Na_2BeF_4

δ - phase (initial). Exposure temperature 20°		ε -phase. Exposure temperature 410°		η -phase. Exposure temperature 470°		θ-phase. Exposure temperature 510°		γ-phase		β -phase		α-phase		α'-phase	
I	*d*, κX	*I*	*d*, κX	*I*	*d*, κX	*I*	*d*, κX	*I*	*d*, κX	*I*	*d*, κX	*I*	*d*, κX	*I*	*d*, κX
6	7,22														
						2	5,98								
		5	5,14												
6	4,86			5	4,52										
		9	4,45												
		10	4,26												
8	4,16					10	4,14								
7	4,02														
		5	3,91	8	3,93	6	3,91					7	3,87		
		5	3,62					8	3,67						
				5	3,542	5	3,528								
		8	3,354												
				2	3,261										
8	3,160														
		7	3,074												
				6	3,035	7	3,035								
						5	2,987								
8	2,886							10	2,915						
				6	2,860										
		8	2,851			6	2,812								
							2,764					9	2,81		
				5	2,700	5				8	2,69			10	2,71
		9	2,680				2,684	9	2,650			9	2,668		
				5	2,610	6	2,601								
		6	2,531			5	2,525								
				5	2,443			10	2,440						
6	2,430														
10	2,368							10	2,365	70	2,37			8	2,35
				5	2,316										
		6	2,294			60B	2,30			30	2,26				
				8	2,211							10	2,198	9	2,216
		9	2,208			10	2,189								
				2	1,174										
5	2,148	5	2,157			6	2,161			100	2,14			9	2,168
7	2,095					3B	2,085			40	2,08				
4	2,040													8	2,033
8	2,004			2	1,973	5	1,966			40	1,95				
		6	1,950	5	1,959										
		5	1,919			5	1,943					9	1,943		
7	1,841					5	1,818	10	1,842					9	1,920
10	1,809	7	1,808												
				6	1,765										
		2B	1,76												
3B	1,744					6	1,749	9	1,752						
						1B	1,715								
5	1,703													7	1,694
6	1,683														
		6	1,672												
4	1,648	2B	1,64	2B	1,64	6	1,631								
		2	1,594			2	1,548	9	1,596						

Footnotes. 1. The coincidence of some of the lines of the ε-phase with the lines of α-Na_2BeF_4 is accidental as follows from the capacity of the ε-phase for tempering. 2. For the value of d for the comparison phases, γ, α and α', we took the average values of measurements from papers [4, 5, 6 and 8] and our own. The relative intensities are taken from our own photographs with a Cu anode. The values of d and I/I_0 for the β-phase were taken from the work of N. A. Toropov [8]. B = Broad.

modification taken for the investigation. If the γ-modification was taken as the starting material, fusion began at 600 – 610° and this temperature corresponds to equilibrium of α-Na_2BeF_4 with the melt, while when δ-Na_2BeF_4 was heated, fusion occurred at about 580°. On some thermograms the fusion effect was diffuse, apparently due to the fact that the substance melted over a temperature range. We determined the solubility of the rhombic and needle-like form of Na_2BeF_4 previously [11]. At first we assumed that the needle-like form of Na_2BeF_4, isolated from solution together with the rhombic form, was the monoclinic modification described by Marignac [1]. The solubility of the needle-like crystals of Na_2BeF_4 (δ-Na_2BeF_4) at 20° equalled 1.7 g per 100 g of solution. The solubility of γ-Na_2BeF_4 was 1.37 g per 100 g of solution. When crystals of the rhombic form, γ-Na_2BeF_4, were introduced into a solution saturated with respect to the needle-like form of Na_2BeF_4(δ), the solubility at first gradually fell and an increase in the amount of rhombic crystals in the solid phase was observed. This indicates that δ-Na_2BeF_4 is a metastable modification.

X-ray investigation of a series of conversions of δ-Na_2BeF_4. By slow evaporation of a solution of Na_2BeF_4 it was possible to obtain comparatively large needle-like crystals of the β-modification of Na_2BeF_4. This made it possible for us to take x-ray rotation pictures of monocrystals of δ-Na_2BeF_4 in a RKU-86 camera on a BSV tube with a Cu anode and to determine by indexing the equatorial reflections of the axial parameter a of the hexagonal lattice, which was found to equal 8.297 ± 0.003 kX. From a rocking x-ray picture on a RKOP camera with subsequent refinement according to a powder photograph) we obtained c = 4.85 ± 0.01 kX. The number of formula units in the elementary cell, z = 3.

Due to the imperfections of the monocrystals we had available, we were unable to determine the diffraction class. No systematic extinctions were noted.

We carried out x-ray investigations of preparations at elevated temperatures in a Lipson and Wilson camera (from the firm "Unicam") [12]. The preparations were placed in thin-walled pyrex capillaries. Fine crystals of the δ-phase, selected under a microscope, were introduced into capillaries without preliminary grinding. The x-ray pictures were takne using a BSV tube with a Cu anode at 30 – 35 kv.

X-ray pictures were obtained at the following temperatures:

1) 20° (initial preparation of δ-Na_2BeF_4), 2) 360° (up to 1st effect), 3) 410° (after 1st effect), 4) 470° (between 2nd and 3rd effects), 5) 510° (between 3rd and 4th effects).

These pictures are reproduced in Fig. 1.

After each photograph at an elevated temperature, a picture was taken of the same preparation at 20°. A comparison of all the x-ray pictures, "hot" and "cold", confirmed the presence of phase conversions, noted on the heating thermograms of the δ-phase,• and their irreversibility. The x-ray pictures taken 1) at temperatures lying close to the corresponding thermal effects and 2) after cooling to t = 20° differed only in a certain shift of the lines, in all probability occurring as a result of anisotropic thermal broadening.

A comparison of the interplanar distances of the high-temperature phases with available literature data for the γ, α', α and β•• modifications of Na_2BeF_4 indicate that the δ-phase may be considered as the initial one for the series of polymorphic varieties it forms and which do not coincide with the similar ones for the γ-Na_2BeF_4 series (see Table 1). It is interesting to note that the series of conversions we investigated do not show a similarity to conversions of Ca_2SiO_4.

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• An x-ray investigation of samples above 545° to confirm the 4th effect was impossible due to strong interaction of the fluoroberyllate with pyrex borosilicate glass.

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SOLUBILITY OF THE SYSTEM Na, Mg ‖ Cl, HCO_3 — H_2O

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(Presented by Academician I. I. Chernyaev November 24, 1958)

Data on solubilities in the system Na, Mg ‖ Cl, HCO_3 — H_2O are extremely limited [1, 2].

We studied the system at a temperature of ~0° and P_{CO_2} = 4 atm. The work was carried out in a "viniplast" autoclave. Into the bottom of the autoclave was sealed a porous glass plate (from a Schott No. 4 filter) and a needle valve, by means of which it was possible to separate the liquid phase and take off samples for analysis. In the lid of the autoclave were set two tubes: one of them, which was sealed with a stopper, was used for loading reagents and passing carbon dioxide to flush air from the autoclave before an experiment and the other was for the input of carbon dioxide from a tank. The lid was also fitted with a thermometer pocket (a thermometer with 0.5° graduations was used for the experiments). The pressure was measured with a manometer on a reducing valve.

TABLE 1

Data on the Solubility of Na, Mg ‖ Cl, HCO_3 — H_2O at P_{CO_2} = 4 atmos and ~ 0°.

Point No.	Composition of solutions, weight%						Jaenicke index			Solid phases
	HCO_3	Cl	Na	Mg	сумма солей	H_2O	HC	Mg	H_2O	
1	0,44	15,71	10,35	—	26,50	73,50	1,60	—	1811,7	$NaHCO_3$+NaCl
2	0,83	15,86	8,67	1,02	26,38	73,62	2,95	18,20	1772,8	$NaHCO_3$+NaCl
3	0,88	14,78	7,19	1,44	24,29	75,71	3,34	27,46	1948,4	$NaHCO_3$+NaCl
4	0,73	14,35	6,59	1,58	23,25	76,75	2,87	31,19	2044,4	$NaHCO_3$+NaCl
5	0,89	16,08	7,04	1,97	25,98	74,02	3,12	34,61	1755,1	$NaHCO_3$+NaCl+$MgCO_3 \cdot 5H_2O$
6	8,35	—	1,22	1,02	10,59	89,41	100,0	61,29	7250,8	$NaHCO_3$+$MgCO_3 \cdot 5H_2O$
7	7,94	0,60	1,36	1,07	10,97	89,03	88,49	59,83	6719,2	$NaHCO_3$+$MgCO_3 \cdot 5H_2O$
8	6,30	1,93	1,60	1,07	10,90	89,10	65,48	55,79	6270,8	$NaHCO_3$+$MgCO_3 \cdot 5H_2O$
9	0,87	15,88	6,96	11,94	25,65	74,35	3,09	34,52	1785,6	$NaHCO_3$+$MgCO_3 \cdot 5H_2O$+NaCl
10	—	25,80	0,13	8,78	34,71	65,29	—	99,24	995,9	NaCl+$MgCl_2 \cdot 6H_2O$
11	0,83	25,28	0,10	8,78	34,99	65,01	1,87	99,39	993,0	NaCl+$MgCl_2 \cdot 6H_2O$+$MgCO_3 \cdot 5H_2O$
12	—	15,55	10,35	—	26,30	73,70	—	—	1818,5	NaCl
13	4,72	—	1,78	—	6,50	93,50	100,0	—	13407,2	$NaHCO_3$
14	7,40	—	—	1,47	8,87	91,13	100,0	100,0	8345,2	$MgCO_3 \cdot 5H_2O$
15	—	25,76	—	8,84	34,60	65,40	—	100,0	998,9	$MgCl_2 \cdot 6H_2O$

During the investigation, the autoclave was placed in a refrigerator of the "Dnepr" type, where the mixture was agitated by means of a shaker. The temperature in the refrigerator was kept constant with an accuracy of ± 0.2°.

As starting materials we used pure-grade magnesium chloride, analytical-grade sodium chloride and pure-grade basic magnesium carbonate. The liquid phase was analyzed for the content of magnesium, chlorine and bicarbonate ions. The amount of sodium was calculated by difference. The solid phase was analyzed microscopically. The system reached equilibrium after two to three days. That equilibrium had been reached was checked by agreement of analysis data on the liquid phase after one day.

Solubility data on the system, expressed in weight percents and by Jaenecke's method, are presented in Table 1 and in Figs. 1 and 2. The equilibrium diagram of the Na, Mg ‖ Cl, HCO_3 — H_2O system contains four

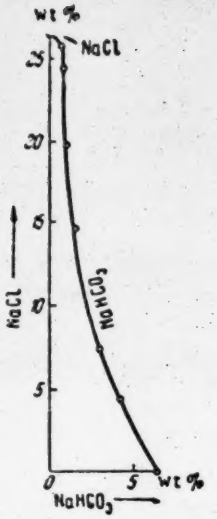

Fig. 1. Ternary system NaCl – $NaHCO_3$ – H_2O at P_{CO_2} = 4 atm. and a temperature of ~0°.

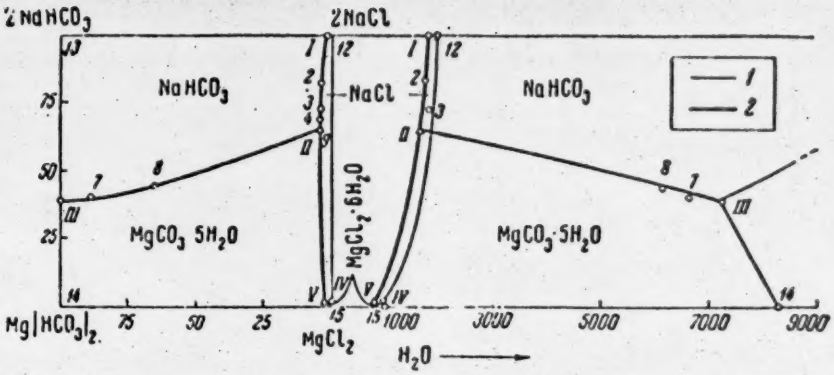

Fig. 2. The quaternary system Na, Mg ‖ Cl, HCO_3 – H_2O at P_{CO_2} = 4 atmos and a temperature of ~0°: 1) lines corresponding to crystallization of one phase; 2) lines corresponding to crystallization of two phases.

salt crystallization fields, namely those of sodium bicarbonate, magnesium carbonate pentahydrate, sodium chloride and magnesium chloride hexahydrate (Fig. 2). It is extremely important that a considerable part (more than 50%) of the area of the diagram is occupied by the sodium bicarbonate field. In the given system, as in the NaCl – $NaHCO_3$ – H_2O ternary system forming part of it, which we studied, sodium bicarbonate is expelled from solutions by sodium chloride (Figs. 1 and 2).

With an increase in P_{CO_2}, the sodium bicarbonate field increases considerably at the expense of the magnesium carbonate field. Here the sodium and magnesium chloride fields remain practically unchanged.

In addition to theoretical interest, the results of investigating the Na, Mg ‖ Cl, HCO_3 – H_2O system also have practical value: they serve as a physicochemical basis for developing a method of preparing sodium bicarbonate through magnesium bicarbonate. Such a method could also be used for the production of potash.

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SYNTHESIS OF DERIVATIVES OF 1, 6-DIOXASPIRO (4, 4)-NONENE-3 BY ELECTROLYTIC ALKOXYLATION OF γ-FURYLALKANOLS

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(Presented by Academician A. A. Balandin January 17, 1959)

The synthesis of spiranes of the 1, 6-dioxaspiro-(4, 4)-nonane group has been accomplished by several methods. They were first obtained starting from butyrolactone, valerolactone, caprolactone and diallylacetone [1, 2, 3]. In 1934 Burdick and Adkins stated that 1, 6-dioxaspiro-(4, 4)-nonane was formed in the hydrogenation of furylacrolein [4]. These spiranes were formed in better yield by the hydrogenation of γ-furylalkanols [5, 6, 8].

The mechanism of this reaction is considered in a series of articles [5, 7].

The present communication is concerned with the formation of bicyclic systems of a similar type by the electrolytic alkoxylation of γ-furylalkanols.

The electrolytic alkoxylation of furanoid substances was discovered in 1952 by Clauson-Kaas [9].

The essence of the method is electrolysis at a temperature below 0° of a solution of the furan compound in an appropriate alcohol with a small amount of ammonium bromide added as electrolyte. The electrolyzer consisted of a nickel cathode and a platinum anode.

The reaction mechanism was not established conclusively.

We substantially improved the construction of the electrolyzer suggested by Clauson-Kaas and this made the apparatus and the method more convenient for practical use. The improvement consisted first of all of replacing the platinum anode by one of carbon.

Experiment showed that alkoxylation of furanoid substances in such a modernized apparatus gave a yield of dialkoxydihydrofuranoid compounds, which in general, was not less than in electrolysis with a platinum anode, as is apparent from Table 1.

It may be recalled that in the same apparatus we were able for the first time to methoxylate acetates of 1-(α-furyl)-propanol-3, 1-(α-furyl)-butanol-3 and n-acetofurfurylaminoethanol and also 1-(α-furyl)-butanone-3 and 1-(α-furyl)-methylpentane.

In undertaking experiments on the electrolysis of solutions of γ-furylalkanols, we started from the hypothesis that due to the spatial proximity of the hydroxyl group in the side chain to the furan ring, with such alcohols together with the normal process of intermolecular alkoxylation, there would occur an intramolecular reaction, accompanied by cyclization.

R=H, CH_3, CH_3—$CH(CH_3)_2$, C_2H_5

R'=respectively, H, H, H or CH_3

TABLE 1

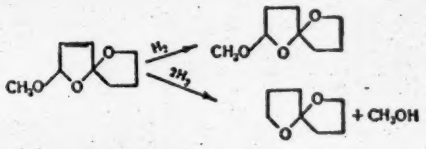
Starting compound	Yield of dimethoxydihydrofuran compound			
	in Glauson-Kaas experiments		in our experiments	
	in % of current	in % amt. start. mat.	in % of current	in % amt. start. mat.
1 Furan	86	73	92	78
2 Sylvan	81	69	85,1	71,4
3 Furfuryl acetate	86	87	81,5	83,3

This hypothesis was confirmed completely by experiment. It was found that electrolysis of 1-(α-furyl)-propanol-3, 1-(α-furyl)-5-methylhexanol-3 and also the tertiary alcohol 1-(α-furyl)-3-methylpentanol-3 in methyl alcohol solution led to the formation of the corresponding 2-methoxy-1, 6-dioxaspiro-(4, 4)-nonene-3 as the main reaction product. The yields varied from 53 to 76% of theoretical, which is considerably higher than in all cases of the formation of 1, 6-dioxaspiro-(4, 4)-nonane and its homologs in the hydrogenation of the corresponding furane alcohols. Data on the properties and the analysis of the four derivatives of 1, 6-dioxaspiro-(4, 4)-nonene-3 thus obtained are presented in Table 2. The structure of these compounds was confirmed experimentally by the following, as well as by the data presented in Table 2.

Hydrogenation of 2-methoxy-1, 6-dioxaspiro-(4, 4)-nonenes under mild conditions (at room temperature, under pressure and in the presence of Raney nickel) led to the formation of 2-methoxy-1, 6-dioxaspiro-(4, 4)-nonane derivatives, whose properties and analysis are presented in Table 3.

Hydrogenation of 2-methoxy-1, 6-dioxaspiro-(4, 4)-nonenes under more drastic conditions (under a pressure of 100 — 120 atmos at 100 — 120° in the presence of nickel on kieselguhr) produced not only hydrogenation of the double bond, but also elimination of the methoxyl group. This gave the previously known, 1, 6-dioxaspiro-(4, 4)-nonane and its homologs.

All these conversions, which completely confirm the structure accepted for 2-methoxy-1, 6-dioxaspiro-(4, 4)-nonenes, are illustrated by the following scheme:



EXPERIMENTAL •

1-(α-Furyl)-propanol-3, 1-(α-furyl)-butanol-3 and 1-(α-furyl)-3-methylpentanol-3 were synthesized as described previously [8, 11].

1-(α-Furyl)-5-methylhexanol-3 was obtained by hydrogenation of furfurylidenemethyl isobutyl ketone in the presence of a copper-chromium catalyst at a temperature of 120° and a pressure of 100 atmos. The yield was 79 — 80% of theoretical. B.p. 116 — 117° (7 mm), n_D^{20} 0.9649, MR_D found: 52.85, calculated: 53.032.

Found %: C 72.93; 72.53; H 10.27; 10.25; OH 9.39; 9.35. $C_{11}H_{18}O_2$. Calculated %: C 72.49; H 9.96; OH 9.32.

The experimental conditions adopted for the alkoxylation and hydrogenation are illustrated by the following examples.

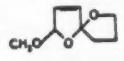
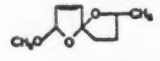
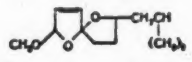
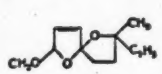
Synthesis of 2-methoxy-7-methyl-1, 6-dioxaspiro-(4, 4)-nonene-3. 58 g of freshly distilled 1-(α-furyl)-butanol-3 and 5 g of ammonium bromide were dissolved in 230 ml of methyl alcohol. The solution was poured into the electrolyzer, cooled to -12° and electrolyzed for 9 hours.

At the end of the electrolysis, the solution was transferred to a flask and to it was added sodium methylate (1.2 g of sodium in 20 ml of methanol). The methanol and ammonia were removed; the sodium bromide precipitate was filtered off and washed several times with ether. After removal of the ether, the residue was fractionated on a vacuum column with an efficiency of 12 theoretical plates.

• With the participation of I. S. Monakhova.

TABLE 2

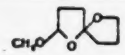
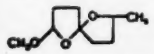
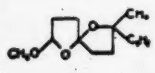
Physical Constants and Analysis of 2-Methoxy-1, 6-Dioxaspiro-(4, 4)-Nonenes-3

Structural formula	B.p., °C	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Elementary composition found % C	found % H	calc. % C	calc. % H	Molec. weight found	Molec. weight calc.	Yield %
	83–84 (10 mm)	1,4650	1,1093	38,94	39,21	61,44 61,50	7,80 8,10	61,52	7,75	163,2 161,8	156,8	53
	72,5–73(5 mm)	1,4572	1,0577	43,80	43,82	63,44 63,76	8,49 8,49	63,51	8,30	178,5 179,3	170,2	76
	81 (2 mm)	1,4570	1,0015	57,73	57,68	67,59 67,89	9,49 9,60	67,89	9,49	202,0 203,7	212,28	75
	92,5–93(6 mm)	1,4563	1,0204	53,06	52,83	66,73 66,81	9,25 9,21	66,64	9,15	195 199	198,25	65

Note: None of the compounds contained hydroxyl groups according to a Terent'ev determination.

TABLE 3

Physical Constants and Analysis of 2-Methoxy-1, 6-Dioxaspiro-(4, 4)-Nones

Structural formula	B.p.., °C	n_D^{20}	d_4^{20}	MR_D found	MR_D calc. %	Elementary composition found % C	found % H	calc. % C	calc. % H	Yield %
	77–78(14 mm)	1,4471	1,071	39,54	39,67	60,93 60,89	8,99 9,02	60,74	8,92	82
	73–74(10 mm)	1,4420	1,026	44,41	44,20	62,97 62,47	9,57 9,33	62,77	9,37	82
	88–89 (10 mm)	1,4447	0,9951	53,53	53,53	65,73 65,62	10,24 10,18	65,97	10,06	79

Synthesis of 2-methoxy-7-methyl-1, 6-dioxaspiro-(4, 4)-nonane. 20.0 g of 2-methoxy-7-methyl-1, 6-dioxaspiro-(4, 4)-nonene-3, 20 ml of absolute ethyl alcohol and 1.5 g of Raney nickel were placed in a rotating steel autoclave of 150 ml capacity.

The initial hydrogen pressure was 100 – 120 atmos and the reaction was performed at room temperature. The hydrogenation was complete after the absorption of 3 liters of hydrogen. The catalyzate was removed from the autoclave, the catalyst removed by filtration and the solvent removed on a water bath. The residue was vacuum distilled.

Synthesis of 2-methyl-1, 6-dioxaspiro-(4, 4)-nonane. 20 g of 2-methoxy-7-methyl-1, 6-dioxaspiro-(4, 4)-nonene was hydrogenated as described previously, but at a temperature of 100 – 120° and an initial pressure of 120 atmos using 20 ml of absolute ethyl alcohol and 2 g of nickel on kieselguhr. The yield was 53 – 54% of theoretical.

The liquid had a peculiar terpene smell. B.p. 162 – 164°; $n_D^{20} = 1.4427$, $d_4^{20} = 0.9911$, MR_D found: 38.01, calculated: 38.03.

Literature data [7]: c.p. 162 – 164°, n_D^{20} 1.4428, d_4^{20} 0.9920.

Under the given conditions, 2-methoxy-1, 6-dioxaspiro-(4, 4)-nonene-3 gave a 56% yield of 1, 6-dioxaspiro-(4, 4)-nonane, which was a liquid with b.p. 82° (60 mm), n_D^{20} 1.4489, d_4^{20} 1.020, MR_D found: 33.16, calculated: 33.41.

The spirane obtained by hydrogenation of furylpropanol had the following constants: b.p. 81 – 82° (60 mm), n_D^{20} 1.4479, d_4^{20} 0.0341.

From 2-methoxy-7-methyl-7-ethyl-1, 6-dioxaspiro-(4, 4)-nonene-3 we obtained a 53% yield of 2-methyl-2-ethyl-1, 6-dioxaspiro-(4, 4)-nonane, which was a liquid with b.p. 103 – 104° (45 mm), n_D^{20} 1.4446 d_4^{20} 0.9638 MR_D found: 46.92 calculated: 47.26.

Literature data [8]: b.p. 102 – 104° (45 mm), n_D^{20} 1.4443, d_4^{20} 0.9614.

Thus, for the first time it was established that under the conditions of electrolytic alkoxylation, primary, secondary and thertiary γ-furylalkanols undergo intramolecular cyclization with the formation of 2-alkoxy derivatives of 1, 6-dioxaspiro-(4, 4)-nonene-3 in good yields. The structure of the latter was proved not only by normal analytical methods, but by their conversion into alkoxy derivatives of 1, 6-dioxaspiro-(4, 4)-nonane and also into previously known 1, 6-dioxaspiro-(4, 4)-nonane and its homologs.

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CATALYTIC POLYCYCLIZATION OF HIGHER ALKANES

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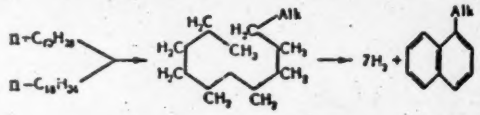
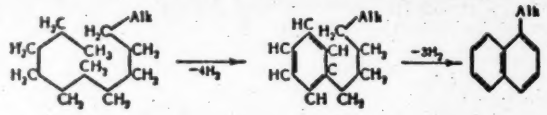
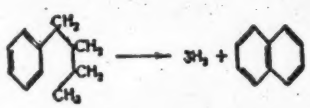
The catalytic dehydrocyclization of alkanes with chains of not less than six carbon atoms in the molecule, which was discovered simultaneously by a group of scientists [1 — 3], has mainly been studied in detail on the example of hydrocarbons of simple composition, giving benzene, toluene or xylene as the end product. However, on the basis of A. A. Balandin's multiplet theory and the sextet model of dehydrogenation catalysis, it might be expected that the higher normal alkanes, beginning with n-decane, should give condensed systems of naphthalene, phenanthrene and more complex polycycles, under conditions favoring dehydrocyclization. In fact we recently observed [4] the formation of naphthalene homologs in the conversions of normal tridecane and hexadecane in the presence of platinized alumina (0.5% Pt) at 425 — 450° under a pressure of hydrogen in a flow system. These conversions, together with other reactions, namely hydrogenolysis and isomerization of alkanes, apparently proceed by the scheme



Under the experimental conditions the α-alkylnaphthalenes may be partially or completely isomerized into the β-form. However, we cannot exclude the possibility that the formation of the condensed system of naphthalene under the given conditions proceeds through the intermediate formation of a substituted benzene with subsequent ring closure of the side chain:



The probability of such a hypothesis is based on the previous observation by one of us [5] that ring closure of the side chain occurs under analogous conditions with n-butylbenzene to give naphthalene:



In the present work we investigated the conversions of n-heptadecane and n-octadecane in the presence of 0.5% Pt, deposited on aluminum oxide and a natural aluminosilicate, gumbrine, and 0.5% Pd on the same carriers

at 450° under a hydrogen pressure of 30 atm, in a flow system [6]. We isolated the starting alkanes from the 190 – 350° fraction of Sokolovogorsk and Mirzaani oils [7] and after careful purification, they had the following properties:

n-$C_{17}H_{36}$ b.p. 302 – 303° (750 mm), n_D^{20} 1.4336 and d_4^{20} 0.7781;

n-$C_{18}H_{38}$ b.p. 316 – 317° (748 mm), n_D^{20} 1.4358 and d_4^{20} 0.7812.

As a result of the experiments, we obtained 8 liquid catalyzates, which were examined in detail by the procedure described previously [4]. The catalyzates were found to contain products of isomerization, hydrocracking and dehydrocyclization of the original alkanes. When the small head fractions boiling up to 100° had been separated from these catalyzates by distillation, the aromatic hydrocarbons were isolated from the residual part of each catalyzate by chromatographic adsorption on ASM grade silica gel. The desorbed mixture of aromatic hydrocarbons was then fractionated on a column with an efficiency of 25 t.p. in a nitrogen atmosphere. According to the constants and optical analysis data, the fractions boiling up to 150° contained toluene and xylenes. It was noted that the catalyzates obtained in conversions of the two alkanes over Pd- and Pt-Al_2O_3 contained not more than 3.5% of toluene and xylenes, while the catalyzates obtained in experiments with Pd and Pt deposited on gumbrine contained up to 9% of these hydrocarbons. The total content of aromatic hydrocarbons in catalytic experiments, carried out in the presence of Pd- and Pt-gumbrine, varied over the range 17 – 22 weight%, while in conversions of the two alkanes on Pd- and Pt-Al_2O_3, their content was only 10.7 – 14.8%.

The aromatic hydrocarbons boiling above 150° had a blue-green fluorescence; they were chromatographed in petroleum ether solution on activated aluminum oxide in two glass columns, containing 200 ml each of fine grained Al_2O_3. Their properties are presented in Table 1. By illumination with UV light with a wave length of 360 mμ, it was found that the mixture of aromatic hydrocarbons (41.0 g), obtained in experiments with Pd- and Pt-Al_2O_3 (column I), had separated into 5 zones, of which four luminesced with a color varying from pale violet to pale blue. A mixture of 76.9 g of aromatic hydrocarbons, obtained in experiments with Pt- and Pd-gumbrine (column II), separated into six zones, of which five (II -- VI) had a sharply expressed luminescence; of these, zone II luminesced with a yellow-green light, zone III with a pale blue, zone IV with blue, zone V violet and zone VI with a pale violet.

TABLE 1

Properties of Fractions Isolated by Chromatographic Adsorption on Al_2O_3 from Mixtures of Aromatic Hydrocarbons with b.p. above 150°

Fraction (zone) No.	Column I					Column II				
	amt. g	b.p. at 731 mm, °C	n_D^{20}	d_4^{20}	m.p. of picrate, °C	amt. g	b.p. at 733 mm, °C	n_D^{20}	d_4^{20}	m.p. of picrate, °C
II	Did not luminesce					4,9	292—293	1,6383	1,0789	116—118
III	3,8	290—295	1,6185	1,0250	112—113	7,3	275—280	1,6323	1,0630	184—186
IV	10,1	289—290	1,5910	0,9940	103—105	8,6	268—269	1,6179	1,0228	109—112
V	11,2	273—275	1,5289	0,9055	89—91	16,1	266—268	1,5070	0,8786	98—100
VI	9,2	266—268	1,4908	0,8666	—	26,6	253—260	1,4870	0,8185	—

The UV absorption spectra* of fraction II, III and IV, isolated from column II, were plotted in isooctane solution on an SF-4 spectrophotometer. As Fig. 1 shows, the spectrum of fraction II consists of several bands with maxima at 255, 320 and 336 mμ and an inflection at 290 – 300 mμ. The intensity of the first maximum exceeded 60,000 units and the region at 305 – 340 mμ had ε = 5000 units. Since the spectra of fractions II and III were very similar to each other and almost coincided, spectral data for fractions II and IV only are presented in Fig. 1.

* The optical analysis was carried out by Yu. P. Egorov and the authors would like to thank him.

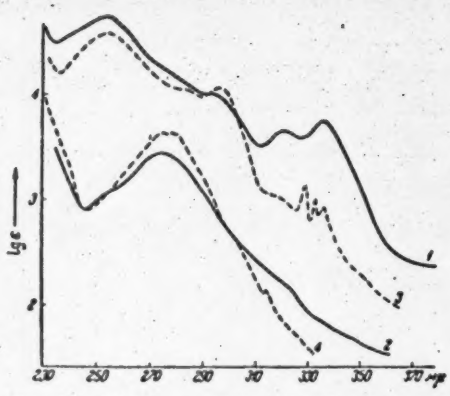


Fig. 1. UV spectra of fractions II and IV in isooctane solution: 1) fraction II; 2) fraction IV; 3) phenanthrene and its closest homologs; 4) α-methylnaphthalene

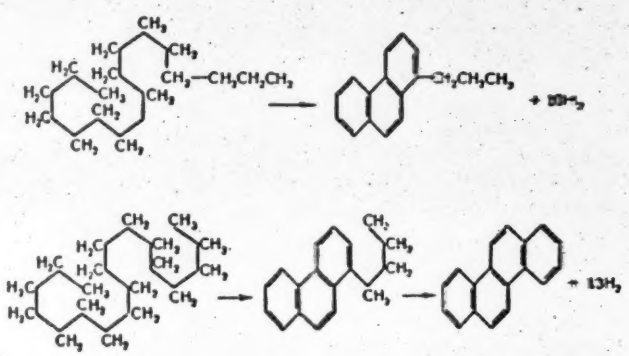
Comparison of the spectra of various polycyclic aromatic hydrocarbons showed that the spectrum of fraction II (Fig. 1, 1) was most similar to the spectrum of phenanthrene and its homologs (Fig. 1, 3). Differences only appeared in the wavelength region of 305 – 340 mμ, where the values of the intensity in our spectrum were high. It might be surmised that the reason for the discrepancy was the presence of a small amount of chrysene, whose spectrum is very similar to that of phenanthrene, but more intense than it.

The spectrum of fraction IV (Fig. 1, 2) in the near and middle ultraviolet had λ_{max} 275 mμ (ε = 2700 units) and λ_{min} 245 mμ. The character of this absorption curve is almost the same as that of α-methylnaphthalene (Fig. 1, 4), though it does not coincide with it. This difference is natural, since we were dealing with fractions consisting of mixtures of aromatic hydrocarbons.

Elementary analysis of fraction II gave the following results:

Found %: C 92.03; 92.30; H 7.90; 7.86 $C_{17}H_{18}$. Calculated %: C 92.67; H 7.33 $C_{18}H_{12}$. Calculated %: C 92.25; H 7.75

Thus, the optical properties and elementary composition of fraction II indicated that it contained alkylphenanthrenes with C_3 – C_4 side chains. However, on the basis of the data obtained it is as yet impossible to decide on the character and the position of these groups. It is probable that fraction II, which possessed a sharply expressed yellow-green luminescence, was a mixture of n-propyl- and n-butylphenanthrenes with a trace of chrysene. Starting from the sextet model of the multiplet theory, their formation may be represented by the following scheme:



Under the conditions we chose, the yield of fraction II, which consisted of phenanthrene homologs, was about 3.5%. At the present time we are investigating the direct catalytic synthesis of condensed aromatic systems by the polycylization of higher alkanes under conditions, which make it possible to obtain them in an individual form in higher yields.

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CATALYTIC DEHYDROGENATION OF ETHANOL ON GERMANIUM

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We previously reported the capacity of germanium for catalyzing a series of reactions of the oxidative-reductive class [1, 2]. To understand the mechanism of semiconductor catalysis, it was desirable to make a more detailed study of the kinetics of some of these reactions on samples of Ge with various types of conductivity and with a wide variation in the concentration of current carriers. In the present article we present the results obtained in the investigation of ethanol dehydrogenation.

The kinetics of ethanol dehydrogenation were studied under static, vacuum conditions in a quartz reactor attached to a vacuum apparatus, over powders with a specific surface of 0.05 — 0.1 m^2/g, prepared by grinding mono- or polycrystalline samples in a mortar in air. The sample of Ge was about 8 — 10 g. Before catalytic experiments, the Ge powders were aged at a temperature of 850 or 650° at 10^{-5} — 10^{-6} mm Hg.

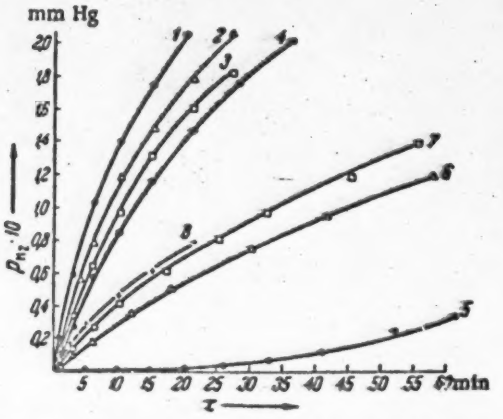

Fig. 1. Kinetic curves of hydrogen evolution in successive experiments after aging at 850° (1 — 4) and after chemisorption of oxygen (5 — 8).

The catalytic dehydrogenation was examined in the range 200 — 270° at an initial ethanol pressure of a few tens of millimeters of Hg, measured with a glass membrane manometer. The composition of the products and the course of the reaction were determined manometrically with freezing out at -78, -134 and -196°. For identification of hydrogen, diffusion through Pd was used in addition.

In successive decompositions of ethanol on Ge samples aged at 850°, a fall in rate was observed (Fig. 1, 1 — 4), which ceased after the fourth experiment. Analysis of the reaction products, obtained on an unstabilized surface, showed that in addition to hydrogen and acetaldehyde, ethylene was present in the gas phase and that the content of the latter fell from experiment to experiment (from 40% with respect to $C_2H_4 + CH_3CHO$ in the first experiment to 3 — 5% in the fourth; data refer to 60% decomposition of ethanol). In all experiments, the hydrogen pressure was equal to the total pressure of acetaldehyde and ethylene with an accuracy of 2 — 3%. These observations indicate that due to the great affinity of a fresh Ge surface for oxygen, an oxygen atom is abstracted from an ethanol molecule by the reaction

$$C_2H_5OH \rightarrow H_2 + C_2H_4 + O_{ads} \qquad (1)$$

TABLE 1

The Logarithm of the Preexponential Factor and the Apparent Activation Energy of the Catalytic Dehydrogenation of Ethanol on Alloyed Samples of Ge.

Sample No.	Additive	Type of conductivity	Percentage content of additive	Concentration of carriers at 20 °C per cc	lg k_0	E, kcal/mole
1	Sb	n	$\sim 10^{-4}$	$\sim 10^{15}$	9,8	27,2
2*	Sb	n	0,02	$5 \cdot 10^{17}$	9,5	27,5
3	Ga	p	$\sim 10^{-4}$	$\sim 10^{15}$	6,5	18,7
4*	Ga	p	0,005	$5 \cdot 10^{17}$	5,9	17,8
5*	Ga	p	0,02	$2 \cdot 10^{18}$	6,4	18,3
6*	Sb, Ga (1 : 5)	p	0,02(Ga)	$2 \cdot 10^{18}$	8,6	23,5
7	Natural Ge	n, p	—	$\sim 10^{14}$	8,5	23,5

(the atomic state of the adsorbed oxygen is adopted provisionally). When the Ge surface is filled with adsorbed oxygen, reaction (I) ceases and, beginning with the fourth experiment, only catalytic dehydrogenation occurs on the Ge powder.

$$C_2H_5OH \rightarrow H_2 + CH_3CHO. \qquad (II)$$

It seemed very interesting to determine the effect of covering the Ge surface completely with oxygen on the catalytic dehydrogenation of ethanol. With this purpose, oxygen was chemisorbed after the fourth experiment and as a result of this, the surface was covered completely. Curves 5 — 8 in Fig. 1 refer to subsequent experiments and represent the kinetics of hydrogen evolution under these conditions. In the first minutes after admission of ethanol vapor into the reaction with oxidized Ge, dehydrogenation hardly occurs (first part of curve 5). The reaction then accelerates (curve 5). The pressure of CH_3CHO, formed by the reaction on the oxidized surface, by far exceeded the hydrogen pressure, indicating that adsorbed oxygen had been removed:

$$C_2H_5OH + O_{ads} \rightarrow H_2O + CH_3CHO \qquad (III)$$

with the portions of the surface freed from oxygen participating in catalytic reaction (II). With several successive experiments on the oxidized surface (curves 5 — 8) a gradual increase in the activity was observed. Thus, in the case of the germanium—ethanol—adsorbed oxygen system a stationary activity of the surface in catalytic dehydrogenation may be approached both from the side of a deoxygenated surface and from the side of a surface completely covered with adsorbed oxygen.

Using the information presented above on the behavior of ethanol on Ge, it was possible to determine reproducibly the kinetics of the catalytic dehydrogenation of ethanol at various temperatures. These data were obtained with a stationary Ge catalytic activity, reached by carrying out a series of successive experiments after aging. By lowering the aging temperature to 650° it was possible to obtain a stable activity even after the second experiment. This did not lead to a change in activation energy. The dehydrogenation was described satisfactorily by an equation of the first order with respect to ethanol. This order was apparent since the order determined from the initial pressures is close to zero. The reason for the discrepancy of the orders is apparently reversible poisoning of the Ge surface by the acetaldehyde formed. Such effects are characteristic of semiconductor catalysis when the signs of the charges of the adsorbed molecules of the starting materials and the product are the same [3].

An investigation of the effect of the type of conductivity and the concentration of the current carriers on the catalytic properties was carried out on powders obtained by grinding samples of Ge alloyed with antimony (n-type) or gallium (p-type). The samples, which contained small amounts of foreign bodies (of the order of 10^{15} per cc), were monocrystalline. Samples with high concentrations of foreign bodies (of the order of 10^{17} – 10^{18} per cc) were prepared by fusing purer samples of Ge with a definite amount of antimony or gallium in quartz tubes in a krypton atmosphere. The concentration of foreign bodies introduced was checked by the electroconductivity (these measurements were made by Yu. N. Rufov). Samples obtained by fusion were polycrystalline and contained a considerable amount of foreign bodies which did not enter the crystal lattice. The type of

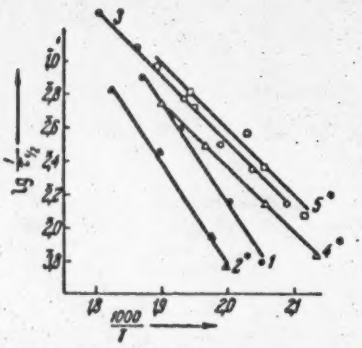

Fig. 2. Temperature dependence of catalytic activity of n-germanium and p-germanium on the dehydrogenation of ethanol

conductivity was determined by thermal "noise". Table 1 gives the electronic characteristics of alloyed Ge samples and also the logarithm of the preexponential factor (k_0) and the apparent activation energy (E) of the catalytic dehydrogenation of ethanol. The stars denote samples alloyed by fusion.

For monocrystalline samples (1, 3) data on the additive content was obtained by calculation from the specific electroconductivity and for samples obtained by fusion (2*, 4*, 5*, 6*), from the weight of the additive. The concentrations of the main current carriers at 20° were obtained by calculation from the specific electroconductivity of the samples (the values 3000 and 500 $cm^2 \cdot v^{-1} \cdot sec^{-1}$, respectively, were taken for the mobility of the current carriers for monocrystalline and fused samples). At the catalysis temperatures a considerable concentration of secondary current carriers appeared in samples 1 and 3, which contained small amounts of additives, as a result of thermal excitation of the lattice. Aging of sample 2* was accompanied by partial sublimation of antimony.

Figure 2 shows Arrhenius lines for catalytic dehydrogenation of ethanol over alloyed Ge samples, calculated for 1 m^2 of surface. Fig. 3 shows a graph of the change in the apparent activation energy in relation to the concentration of the main current carriers in the volume of Ge, constructed from the data in Table 1. It is noticeable that a sharp increase in the activation energy occurs at the transition from hole to electron conductivity and this amounts to 8 — 9 kcal/mole. From the data in Table 1 it follows that the preexponential factor changes symbasically with the activation energy, i.e., the action of the Sb and Ga additives had a modifying character. The whole change in activation energy at the conductivity-type transition was complete at low carrier concentrations. An increase in the carrier concentration from 10^{15} to 10^{18}, which gave a considerable displacement in the Fermi level in the volume of the Ge, had no effect on the value of the activation energy and, as follows from Fig. 2, did not lead to an increase in catalytic activity. Until recently it was thought that a change in the position of the Fermi level in the volume of a semiconductor must have a strong effect on the catalytic activity [4, 5].

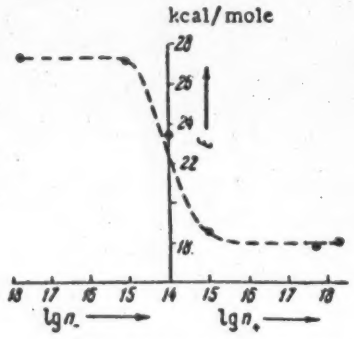

Fig. 3. Dependence of the apparent activation energy of ethanol dehydrogenation on the concentration of main carriers in Ge

The introduction of considerable amounts of antimony into Ge led to a sharp fall in the catalytic activity. From Fig. 2, it follows that sample 2, which contained 0.02% Sb, had the lowest activity of the alloyed samples studied. Increasing the Sb content to 0.06% led to complete loss of catalytic activity.

With sample 6*, which contained Sb and Ga in a ratio of 1 : 5 (considering foreign bodies entering the crystal lattice) and possessed hole conductivity, we found a higher activation energy than for hole samples containing only Ga. This indicated the possibility of selective accumulation of Sb in the surface layer.

The results presented shed some light on the widely discussed problem of the catalytic equivalence of n- and p-semiconductors. In the dehydrogenation of ethanol studied it can be stated with some certainty that the activation energy of the reaction on p-germanium is considerably less than that on n-germanium. One should be careful in extending this conclusion to other reactions, though data obtained by Schwab et al. for the hydrogenation of ethylene and the decomposition of formic acid on Ge [6, 7] and which became known to us when our work on catalysis on alloyed Ge samples was complete, agree qualitatively with our results. Regrettably, the material published by the authors mentioned contained a very superficial description of both the investigation procedure and the kinetics of the reactions studied, which makes it difficult to evaluate the reliability of the results obtained.

For a more complete understanding of the role of the type of conductivity in oxidative-reductive heterogeneous catalysis it is necessary both to extend the range of reactions studied and to investigate more thoroughly

the catalytic processes in conjunction with data on the change in the electronic characteristics of the surface during the reaction.

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PENTAETHANODIFERROCENE

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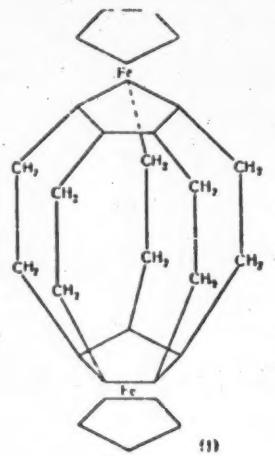
In continuing a study of the alkylation of ferrocene under Friedel-Crafts conditions with alkyl and alkylene halides, we reacted ferrocene with a large excess 1, 2-dichloroethane without additional solvent and under drastic conditions.

As a result, instead of the products we obtained previously, namely, diferrocenylethane and relatively high-molecular resins, containing several ferrocene nuclei in their structure-linked by CH_2-CH_2 bridges, we obtained a series of polyethanopolyferrocenes, which did not contain halogen, were soluble in chloroform and benzene and insoluble in methanol and could be separated by solubility in ether.

All these substances together with unreacted ferrocene were extracted from the reaction mixture with benzene after removal of the dichloroethane by distillation. The mixture was resolved by means of the differences in the solubilities of the polyethanopolyferrocenes in ether. The substance with the lowest molecular weight, which had a decomposition point of 130°, was separated by solution in a small amount of ether and precipitation with methanol and purified by repeated similar precipitations and chromatography on aluminum oxide. According to analysis, the polyethanopolyferrocene thus obtained contained 2 ferrocene nuclei and 5 ethane bridges. Its molecular weight (cryoscopically 545 and 568, calculated 502) confirmed the fact that it was pentaethanodiferrocene. Since the infrared spectrum showed the presence of unsubstituted cyclopentadienyl nuclei of ferrocene (frequencies 1000 and 1100 cm^{-1}), apparently the only possible structure for this substance is represented by model (I).



(I)

This structure was confirmed by the fact that the IR spectrum (LiF prism; without solvent) did not contain the frequencies 2960 and 2870 cm^{-1}, which are characteristic of methyl groups, and did contain the frequencies 2928 and 2850 cm^{-1} (CH frequencies of CH_2 groups). Thus, the ethane bridges are not destroyed by aluminum chloride.

Further confirmation is derived from the increased density of the substance (d_4^{20} = 1.461) in comparison with ferrocene (d_4^{20} = 1.349), which corresponds to dense packing of two ferrocene residues with a separation between the cyclopentadienyl planes connected by CH_2-CH_2 bridges less than in the ferrocene crystal.

This density corresponds approximately to that calculated from the model. The theoretical volume of the molecule was calculated for the model of substance (I) [3]. Here it was assumed that the interatomic valence distances in the ferrocene nuclei were the same as in ferrocene and that those in the ethylene groups were normal for an ordinary bond (1.54 A°). The intermolecular radius of carbon atoms was also taken as the normal value (1.8 A°). Knowing the volume and the weight of the molecule and assuming that the packing coefficient in the crystal was close to 0.7, we calculated the probable density of the substance and this was found to be 1.46 g/cm^3.

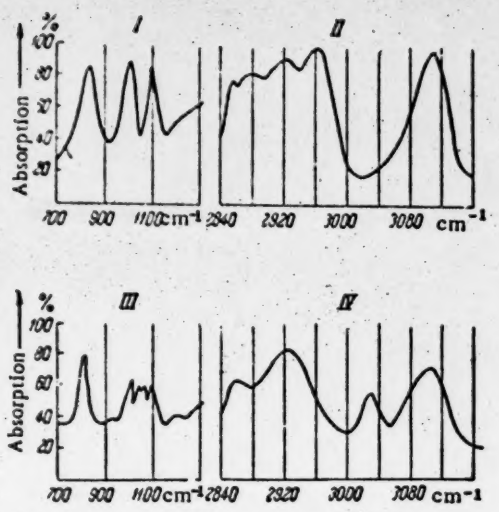


Fig. 1. IR spectra of ferrocene (I), ethylferrocene (II) and pentaethanodiferrocene (III and IV).

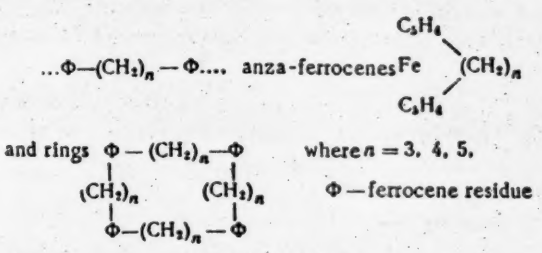
The greater density of substance (I) in comparison with ferrocene, which is too high for a substance in which the content of the relatively heavy atoms (Fe) is small, indicates that the carbon atoms in the molecule are packed extremely closely.

At room temperature, pentaethanodiferrocene did not give x-ray pictures of a crystalline substance and this may be connected with interorientation of the barrel-shaped molecules along the long axis. Laborious work is still required to confirm the structure of pentaethanodiferrocene by chemical methods. By way of preliminary data, bromination [4] gave pentabromocyclopentane.

Polyethanoferrocenes with molecular weights (cryoscopically in benzene) of about 1000 and 2000, containing 4 and 8 ferrocene residues, were less soluble in ether and could be isolated by fractional precipitation with methanol. In analysis they were similar to the previous substance and were possibly 2 and 4 similar molecules linked with ethane bridges.

Actually the IR spectra of the high-molecular weight products showed a fall in intensity of the absorption bands in the regions of 1000 and 1100 cm^{-1}, i.e., a fall in the number of free cyclopentadiene rings in a given amount of material.

Very recently Luttringhaus and Kullick [2] used the reaction of dimetallic derivatives of dicyclopentadienyl- - α-ω-alkanes with ferric chloride to obtain very small yields (0.025 – 0.053%) of ferrocene derivatives, containing polymethylene chains, namely, substances of three types:



Ferrocene and dichloroethane. 40 g of dry ferrocene was dissolved in 300 ml of dry, distilled dichloroethane and the solution gradually heated to 60° with continuous stirring, while 10 g of anhydrous aluminum chloride was added. Stirring at 60° was continued for 5 hours. The mixture was left overnight at room temperature and then stirred and heated at 60° for 6 hours on each of three days. Each day a further 5 g of anhydrous aluminum chloride was added. After decomposition with water and evaporation of excess dichloroethane, the mixture was reduced with an aqueous solution of sodium sulfite and extracted with benzene. After removal of the benzene, the unreacted ferrocene was separated from the reaction products by steam distillation (17 g). The residue was treated with 25 ml of ether and the solution obtained was diluted with ten times its volume of methyl alcohol. A light yellow powder of I (yield 1.9 g; 3.5%) was obtained.

Found %: C 71.64; 71.50; H 6.25; 6.30; Fe 21.70; 21.90 $C_{30}H_{30}Fe_2$. Calculated %: C 71.74; H 6.02; Fe 22.25.

The substance was dried in vacuum (1 mm) for 15 hours at 80°. Mol. weight (determined cryoscopically in benzene): found 545; 568; calculated 502. Density d_4^{20} = 1.461 (in methyl alcohol).
A Beilstein test for chlorine was negative.

The substance was readily soluble in benzene, ether and chloroform, difficultly soluble in ethyl and methyl alcohols and insoluble in water.

The residue after the ether extraction at room temperature, was treated with ether in a Soxhlet apparatus. The ether extracts were evaporated to 50 ml and diluted with ten times its volume of methyl alcohol. We obtained a yellow powder of II (1.1 g). The decomposition point was about 180°.

Found %: C 72.38; 72.17; H 6.43; 6.44; Fe 21.95; 21.68 $C_{64}H_{64}Fe_4$. Calculated %: C 72.73; H 6.12; Fe 21.15.

The substance was dried in vacuum (1 mm) at 80° for 15 hours. The molecular weight (cryoscopically in benzene) was 1030; 980. Calculated for $C_{64}H_{64}Fe_4$ — 1056. The proposed structure for product II is

$$\Phi(CH_2CH_2)_6\Phi(CH_2CH_2)_6\Phi(CH_2CH_2)_6$$

and other possible isomers.

The residue in the thimble of the Soxhlet apparatus was dissolved in 25 ml of benzene and precipitated with ten times the volume of methyl alcohol. We obtained 1.2 g of a brown powder. The analysis was identical to that of substance II. The molecular weight, determined cryoscopically, in benzene, was 2300.

The theoretical calculation of the density of substance I was kindly carried out at our request by O. V. Starovskii under the direction of Prof. A. I. Kitaigorodskii. The IR spectra were measured by N. A. Chumaevskii in the laboratory of Academician I. V. Obreimov. The authors are grateful to all these people.

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THE NATURE OF LINK'S SALT

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(Presented by Academician B. A. Arbuzov February 10, 1959)

For more than a hundred years investigators have been occupied with the problem of preparing dolomite by direct precipitation from solutions of calcium and magnesium salts. It has served as a stimulus for a large amount of experimental work, which, however, has not resulted in any definite conclusions. The opinion of certain authors that their experiments had yielded dolomite required strict experimental testing since the methods they used for identification of the substance obtained (quantitative composition, low solubility in dilute CH_3COOH and, rarely, refractive index) could not give a correct indication of its nature. In repeating some of the experiments, our attention was attracted by Link's salt. This was obtained by directly mixing solutions of Ca and Mg salts and NH_4HCO at room temperature and appeared as a gelatinous precipitate, which rapidly crystallized when heated to 30–40° and slightly more slowly at room temperature to give spherulites with a low solubility in dilute CH_3COOH in the cold. Its quantitative composition is close to that of dolomite.

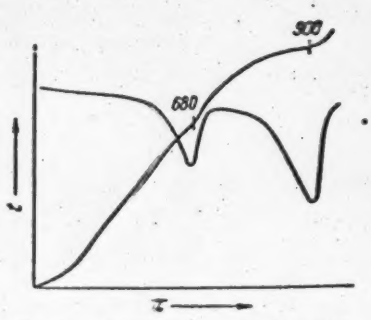

Fig. 1. Thermogram of Link's salt.

However, the variable composition obtained for the precipitate, depending on the initial concentration of the salts and the experimental temperature, the absence of rhombohedra with refractive indices corresponding to dolomite and the variable degree of solubility in CH_3COOH seemed to refute Link's opinion that his salt was none other than dolomite. These salts therefore became known as Link's mixed salts.

The gel we obtained by Link's method [1] was only calcite according to quantitative composition and apparently had a high activity, which promoted the precipitation of magnesium carbonate during crystallization of the gel. Beginning two hours after mixing of the solutions, the magnesium-enriched precipitate gradually reaches a composition close to that of dolomite, namely $MgCO_3$ up to 33% and $CaCO_3$ up to 67%.

If the starting concentration of $CaCl_2$ in our experiments was decreased by a factor of two without a change in the concentration of Mg salts, then only half of the amount of Mg salts precipitated in the form of Link's salt and the rest of them precipitated as nesquehonite. This confirms the hypothesis that it is precisely the $CaCO_3$ gel which facilitates subsequent precipitation of the Mg in the form of Link's salt. If separately prepared and washed $CaCO_3$ gel was placed in a solution of magnesium salts, in this case it did not posses this increased activity and the whole of the Mg precipitated in the form of nesquehonite.

The heating curves of Link's salt, washed free from Cl' and SO_4'' ions, had two endothermal effects, the first (680°) slightly bellow the decomposition point of dolomite (740°) and the second, corresponding to the dissociation temperature of calcite (900°) (Fig. 1).

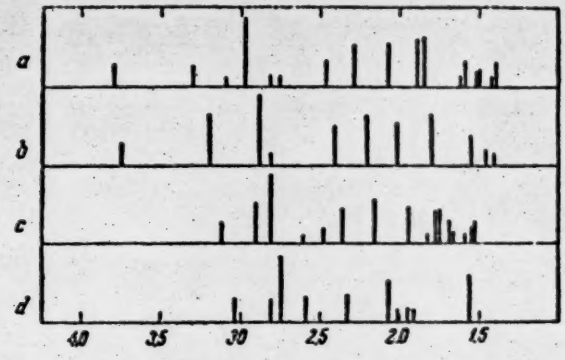

Fig. 2. X-ray pictures of salts: a) calcite ($CaCO_3$), b) Link's salt, c) Shishim dolomite ($CaCO_3 \cdot MgCO_3$), d) magnesite ($MgCO_3$).

A comparison of x-ray pictures of Link's salt with those of Shishim dolomite indicated that Link's salt was a solid solution of calcite in dolomite, since the lattice parameters of a sample of Link's salt differed somewhat from calcites and dolomites, but were more similar to dolomite (Fig. 2).

The spread of the lines on the x-ray pictures and the reduction of the first endothermal effect on the heating curve might be caused by both fine crystallinity and poor formation of crystals and by the nonequilibrium state of the system.

At winter temperatures, the surface of a mixture of dolomite with calcite is more stable than calcite-dolomite solid solutions [2 – 4], which is confirmed by the wide distribution of dolomite in sedimentary rock and by thermochemical data [5].

Thus, it might be expected that under normal conditions with the passage of time, the less stable calcite-dolomite solid solution would change into the more stable form, namely a mechanical mixture of dolomite with calcite.

This would not require an increase in temperature, which is considered necessary by some authors [2], for raising the mobility of the ions and the correct distribution of Ca^{++} and Mg^{++} ions in the dolomite lattice [2].

In the rapid crystallization of carbonates, this route is possible also in nature, as is indicated by the very extensive paragenesis of calcite with dolomite. However, a slow interaction of solutions by diffusion may give directly a stable mechanical mixture of calcite with dolomite.

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DESTRUCTIVE ALKYLATION OF BENZENE BY PROPANE

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The interaction of paraffinic and aromatic hydrocarbons is one of the least studied fields of hydrocarbon chemistry. Nonetheless, the reactions between these classes of compounds may open up new routes to the preparation of various aromatic substances and also help to elucidate the nature of catalytic conversions.

As follows from patents [1, 2], paraffinic hydrocarbons alkylate benzene in the presence of hydrogen fluoride, boron trifluoride and mixtures of them. In patents it is emphasized that paraffins containing not less than five carbon atoms in the chain are suitable for this process. The destructive alkylation of benzene with isooctane proceeds in the presence of aluminum and zinc chlorides [3] at 25 – 75° with the formation of tert.-butylbenzene and isobutane. It was also reported that the destructive alkylation of benzene proceeds in the presence of an aluminosilicate catalyst [4]. The alkylation of benzene with ethane occurs to a small extent on nickel deposited on alumina [5]. This yielded 5% of toluene and the catalyzate did not contain ethylbenzene. Finally, it should be noted that in the presence of nickel on kieselguhr, according to the communication of Ipatieff and Monroe [6], at a pressure of 410 – 545 atmos and a temperature of 372° toluene is formed from benzene in 12 – 15% yield on the benzene passed. The introduction of methane into the reaction mixture raises the yield of toluene to 15 – 20%. On the basis of these works and especially if we consider that under a pressure of hydrogen, a nickel catalyst will selectively demethylate paraffinic hydrocarbons and the side chains of aromatic hydrocarbons [7 – 9], it might be expected that toluene would be formed by the interaction of benzene with various paraffinic hydrocarbons under pressure in the presence of nickel catalysts.

Preliminary experiments which we carried out confirmed the possibility of forming toluene by the interaction of benzene with a series of normal paraffinic hydrocarbons (heptane, hexane, butane and propane) in the presence of a nickel catalyst at a pressure of 60 atmos, i.e. at a considerably lower pressure than that in the work cited above [6]. We studied in more detail the interaction of benzene with propane on nickel deposited on kieselguhr and this is described in the present article.

EXPERIMENTAL

The experiments were performed on an apparatus, whose reactor (stainless steel ÉYal-T; internal diameter 2.6 cm) was loaded with 200 ml of catalyst (nickel on kieselguhr). Fresh catalyst was reduced before the experiment in a stream of hydrogen at atmospheric pressure and 350° for 4 – 5 hours.

A prepared equimolecular mixture of benzene (b.p. 80.1° at 760 mm Hg; $d_4^{20} = 0.8787$; $n_D^{20} = 1.5010$) and propane was introduced into the reactor at the given pressure and a volume rate of 0.18. The catalyzates obtained were distilled on a column with an efficiency of 35 t.p. Fractions boiling above benzene were liquid reaction products, which we provisionally named "alkylbenzenes". However, these products also contained solid aromatic hydrocarbons such as naphthalene and, apparently, diphenyl.

The results of experiments at 400°, presented in Table 1, showed that with an increase in pressure, the yield of alkylbenzenes, calculated on the benzene passed, fell from 32 to 30 weight %.

TABLE 1

Effect of Pressure on the "Alkylbenzene" Yield (aromatics boiling above benzene) From a Propane-Benzene Mixture. Experimental Temperature 400°, Volume Rate 0.18

Exp. No.	Pressure, atmos	C_6H_6 passed, g	Yield of alkylbenzenes on benzene, weight %
28	60	45	32
29	80	35.0	32
27	100	45.0	31
30	120	85.0	30

The effect of temperature on the yield of catalyzate and the content of alkylbenzenes in the latter was determined at 60 atmos (see Table 2). When the temperature was increased from 350 to 450°, the yield of alkylbenzenes on the benzene passed decreased from 28 to 21 weight % in experiments No. 35_1 —$_3$ and from 38 to 25 weight % in experiments Nos. 37 and 38. Experiments 35_1, 35_2 and 35_3 were carried out on the same day on regenerated catalyst with hydrogen flushing of the latter in the periods between experiments when the new temperature was being established. Experiments 37 and 38 were each on fresh portions of catalyst. Decreasing the temperature to 300° produced a sharp fall in the yield of alkylbenzenes in the catalyzate to 10 weight %.

During the prolonged experiment No. 14 (pressure 60 atmos, temperature 400°) it was found that the catalyst was poisoned during operation. The yield of alkylbenzenes, calculated on benzene passed, systematically decreased (see Table 3): over the first two hours of the experiment, the yield of alkylbenzenes was 27%; the yield of alkylbenzenes over the last two hours operation at the end of the experiment (i.e. during the working period from 18.4 hours to 20.7 hours from the beginning of the experiment) equalled 18%.

The activity of the catalyst, poisoned in experiment No. 14 after 21 hours continuous operation, could be increased by passing hydrogen throughit at 100 atmos and 400° for four hours; after this treatment, the yield of alkylbenzenes in the catalyzate of a two-hour experiment rose to 23%.

It was found possible to regenerate the nickel catalyst in a stream of air if the temperature in the oxidation zone was not allowed to rise above 400°. However, such regeneration of the catalyst required two to three days. The catalyst was again reduced before the experiment. It is most probable that during the regeneration of the nickel catalyst with hydrogen at 400° and 100 atm., there occurs hydrocracking of the carbon deposits on the catalyst.

TABLE 2

Effect of Temperature on the Yield of "Aklylbenzenes" (aromatics boiling above 80°) From a Propane-Benzene Mixture, Pressure 60 atmos, Volume Rate 0.18

Exp. No.	Temp., °C	C_6H_6 passed, g	Yield of alkylbenzenes on benzene, weight %	Exp. No.	Temp., °C	C_6H_6 passed, g	Yield of alkylbenzenes on benzene, weight %
35_1	350	23.0	28	37	450	69.0	25
35_2	400	23.0	28	38_1	350	23.0	38
35_3	450	23.0	21	38_2	300	22.0	10

In addition to the formation of substances boiling above benzene from a mixture of propane and benzene, hydrogenation of the latter occurred to a small extent and the cyclohexane formed was isomerized into methylcyclopentane. However, not once did we observe any noticeable amount of liquid products of hydrocarbon cracking.

The temperature at which the head fractions began to boil in distillations of catalyzate on columns never fell below the boiling point of an azeotropic mixture of benzene and methylcyclopentane.

The introduction of hydrogen into the reaction mixture (60 atmos, 400°) decreased the alkylbenzene content of the catalyzate to 10 – 13 weight %. In distillations on a column of the catalyzate obtained from a propane-benzene mixture in the presence of hydrogen, low-boiling hydrocarbons (beginning to boil at 34°) were detected. An investigation of the reaction products revealed paraffinic hydrocarbons (hexanes), indicating the occurrence of hydrocracking and hydrogenolysis of naphthenes, obtained as a result of hydrogenation and isomerization of aromatic hydrocarbons.

TABLE 3

Effect of Experiment Duration on the Catalyst Activity. Experiment Temperature 400°, Press. 60 atmos, Volume Rate 0.18.

Exp. No. Exp. No.	Operation time hours	C_6H_6 passed, g	Yield of alkylbenzenes on benzene, weight %
14	0– 2.0	36	27
	2.0– 4.3	31.9	26
	4.3– 6.9	30.9	23
	6.9– 8.9	25.6	21
	8.9–11.3	30.0	23
	11.3–13.8	31.2	23
	13.8–16.0	31.2	19
	16.0–18.4	31.2	16
	18.4–20.7	31.2	18
15*	0– 2.5	34.4	23

* After regeneration with hydrogen (100 atmos) and 400° for 4 hours.

A comparison of the data of the present work with the results of investigations of the hydrogenolysis of hydrocarbons under a pressure of hydrogen, carried out by one of us and E. M. Terent'eva [10] indicates that a pressure of hydrogen hinders not only rupture, but also the formation of C – C bonds in the presence of nickel catalysts. It is possible that this phenomenon is connected with a decrease in the activated adsorption of the saturated hydrocarbons under the effect of the hydrogen pressure.

To determine the composition of the products formed from propane-benzene mixtures in 18 – 38% yield, all the catalyzate fractions boiling above benzene were combined and distilled on the same column. The distillation curve, beginning with the toluene fraction is presented in Fig. 1. We isolated 77 weight % (calculated on the reaction products) of toluene fraction, containing 95% of toluene (unsaturateds were absent) and having the following constants: b.p. 109.0 – 111.0°; $d_4^{20} = 0.8593$; $n_D^{20} = 1.4923$; we then distilled 9 weight % of xylene fraction, 3% of propylbenzene fraction and 9% of hydrocarbons boiling above 170°. From a comparison of the distillation data and the results of examining the ultraviolet absorption spectra of the fractions at low temperatures *, it follows that the xylene fraction contained ethylbenzene in addition to xylene and that the propylbenzene contained isopropylbenzene.

When benzene alone was passed under the same conditions as for the propane-benzene mixture, the yield of alkylbenzenes was only 8 – 14%. The reaction products from benzene alone contained 82% of a toluene fraction (see Fig. 2) and 16% of hydrocarbons boiling above 170°; the intermediate fraction, containing xylenes, represented a total of 2%. Thus, the yield of toluene from the propane-benzene mixture was, on an average, 23 weight %, calculated on the benzene, and the average yield of toluene from pure benzene equalled 9%. Thus, 2 – 3 times as much of products boiling above benzene were formed in the presence of propane as when benzene alone was passed through the catalyst. This phenomenon apparently arises for two reasons: 1) destructive alkylation of benzene by propane, which proceeds together with autoalkylation of benzene (proceeding during the passage of benzene alone) and 2) a decrease in the poisoning of the nickel catalyst when the reaction was performed in a stream of propane [11].

Since the catalyzates from propane-benzene mixture contained more than 3% of propyl- and ethylbenzene fractions and no appreciable amounts of these hydrocarbons were found in the catalyzate from benzene alone (in the work of Ipatieff and Monroe [6] the liquid reaction products contained up to 98% of toluene, and the authors did not observe the presence of propyl- or ethylbenzene), it must be assumed that under our conditions the direct

* The spectral investigation of the fractions was carried out by V. L. Broude in the Institute of Physics, Acad. Sci. Ukrainian SSR and the authors would like to thank him for this.

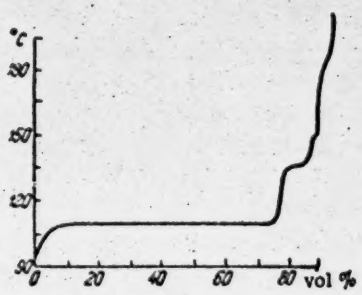

Fig. 1. Distillation curve of the mixture of fractions boiling above benzene from the catalyzates from propane-benzene mixture.

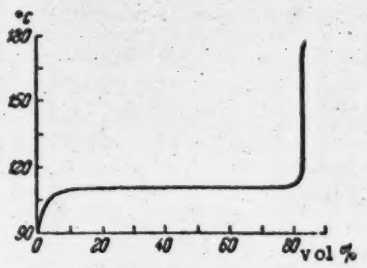

Fig. 2. Distillation curve of the mixture of fractions boiling above benzene from the benzene catalyzates.

alkylation of benzene by propane also occurred; it is possible that propylbenzene formed was partly demethylated into ethylbenzene and then into toluene.

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ORGANOBORON COMPOUNDS. REACTION OF TRIALKYLBORONS WITH COMPOUNDS CONTAINING LABILE HYDROGEN

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(Presented by Academician B. A. Kazanskii February 9, 1959)

The reactivity of aliphatic boron compounds with respect to compounds with active hydrogen has been studied very little. The compound that has been studied mainly is trimethylboron, which reacts with water [1], methylamine [2], ammonia [3], aniline [4], diamines [5], ethylene glycol and pyrocatechol [1] under drastic conditions (at 200 – 300° under pressure) to form methane and the corresponding methyl derivatives of boron. It is also known that triethylboron reacts when heated with β-haloethyl alcohols [6] and that tri-n-butylboron is converted by boiling hydrobromic acid into dibutylboric acid and by dry hydrogen bromide, into dibutylboron bromide [7]. One of us and F. B. Tutorskaya showed that triallylboron had an unusual sensitivity to reagents containing labile hydrogen [8]. It reacted with water, alcohols and amines, even at room temperature, and one or two of the allyl radicals were replaced by the corresponding groups.

In connection with what has been said, it seemed very interesting to study the behavior of higher trialkylborons with respect to various reagents with labile hydrogen and to determine the effect of the nature of the starting materials on the rupture of the boron-carbon bond.

We studied the reactions between tri-n-propyl-, triisopropyl-, tri-n-butyl-, triisobutyl- and triisoamylboron, on the one hand, and water, alcohols, phenol, amines and mercaptans, on the other. It was found that at 160 – 170°, the higher trialkylborons reacted vigorously with water to give dialkylboric acids (I), which were isolated in 65 – 71% yields by distillation in the form of their anhydrides (see Table 1). The reaction was accompanied by the formation of olefinic hydrocarbons and hydrogen and also of saturated hydrocarbons. The course of the process may be illustrated by the scheme

$$R_3B + H_2O \rightarrow R_2BOH + RH + R_{-H} + H_2$$

The relative amounts of hydrocarbons and hydrogen formed in the reaction depended on the experimental conditions. When the water was added portionwise to heated trialkylboron, olefinic hydrocarbons and hydrogen were formed predominantly (see Table 1) and when an equimolecular mixture of reagents was heated, more saturated hydrocarbon was obtained than olefinic.

Under the same conditions, trialkylborons reacted with aliphatic alcohols or phenol to give a 65 – 80% yield of alkyl or phenyl esters of dialkylboric acids (II), saturated and olefinic hydrocarbons and hydrogen.

$$R_3B + R'OH \rightarrow R_2BOR' + RH + R_{-H} + H_2$$

(II)

$R' =$ alkyl, C_6H_5

TABLE 1

Exp. No.	R_3B	Mole	R'YH	Mole	Amount of gaseous reaction products, in moles: C_nH_{2n+2}	C_nH_{2n}	H_2	Reaction product
1	$(i\text{-}C_3H_7)_3B$	0,077	H_2O	0,077	0,018	0,048	0,047	$[(i\text{-}C_3H_7)_2B]_2O$
2	$(n\text{-}C_3H_7)_3B$	0,091	H_2O	0,094	0,013	0,071	0,075	$[(n\text{-}C_3H_7)_2B]_2O$
3	$(i\text{-}C_3H_7)_3B$	0,112	H_2O	0,112	0,003	0,101	0,102	$[(i\text{-}C_3H_7)_2B]_2O$
4	$(i\text{-}C_4H_{11})_3B$	0,070	H_2O	0,080	—	0,051	0,055	$[(i\text{-}C_4H_{11})_2B]_2O$
5	$(n\text{-}C_4H_9)_3B$	0,066	C_2H_5OH	0,066	0,033	0,026	0,028	$(n\text{-}C_4H_9)_2BOC_2H_5$
6	$(n\text{-}C_4H_9)_3B$	0,053	$n\text{-}C_4H_9OH$	0,053	0,010	0,040	0,039	$(n\text{-}C_4H_9)_2BOC_4H_9\text{-}n$
7	$(n\text{-}C_3H_7)_3B$	0,075	C_6H_5OH	0,075	0,012	0,052	0,057	$(n\text{-}C_4H_9)_2BOC_6H_5$
8	$(n\text{-}C_3H_7)_3B$	0,054	$i\text{-}C_3H_7NH_2$	0,061	0,0093	0,0378	0,0394	$(n\text{-}C_3H_7)_2BNHC_3H_7\text{-}i$ (*)
9	$(n\text{-}C_3H_7)_3B$	0,054	$nC_4H_9NH_2$	0,06	—	—	—	$(nC_3H_7)_2BNHC_4H_9\text{-}n$
10	$(n\text{-}C_3H_7)_3B$	0,071	$C_6H_5NH_2$	0,078	0,0232	0,0473	0,0478	$(nC_3H_7)_2BNHC_6H_5$
11	$(n\text{-}C_3H_7)_3B$	0,079	$n\text{-}C_3H_7SH$	0,065	0,0760	0,0004	—	$(nC_3H_7)_2BSC_3H_7II$
12	$(n\text{-}C_3H_7)_3B$	0,110	$n\text{-}C_4H_9SH$	0,11	0,0736	0,0023	0,0020	$(n\text{-}C_4H_9)_2BSC_4H_9\text{-}n$ (*)
13	$(i\text{-}C_3H_7)_3B$	0,076	$n\text{-}C_4H_9SH$	0,076	0,0568	0,0044	0,0006	$(i\text{-}C_3H_7)_2BSC_4H_9\text{-}n$
14	$(i\text{-}C_4H_{11})_3B$	0,065	$n\text{-}C_4H_9TH$	0,0668	0,0464	0,0053	0,0053	$(i\text{-}C_4H_{11})_2B\text{-}C_4H_9\text{-}n$
15	$(n\text{-}C_4H_9)_3B$	0,0658	C_6H_5SH	0,066	0,031	0,014	0,014	$(n\text{-}C_4H_9)_2BSC_6H_5$

Exp. No.	Yield in %	B.p. °C/mm	d_4^{20}	n_D^{20}	Analysis: found in % C	H	B	calculated in % C	H	B
1	59,5	77—78/8	0,7761	1,4222	69,15	13,39	10,33	68,64	13,44	10,31
2	71,1	139—140/12	0,7903	1,4270	—	—	—	—	—	—
3	67,1	111—112/9	0,7723	1,4230	72,01	13,38	8,25	72,22	13,64	8,13
4	65,3	143—144/4	0,7934	1,4331	74,43	13,61	6,65	74,55	13,77	6,72
5	65	79—81/20	0,7886	1,4105	—	—	6,40	—	—	6,33
6	80,4	92—94/8	0,8077	1,4222	—	—	—	—	—	—
7	75,8	118—119/7	0,8798	1,4760	76,99	10,62	5,13	77,08	10,63	4,96
8	78,5	72,5°/11	0,7724	1,4250	—	—	—	—	—	—
9	56	92—93/8	0,7758	1,4302	73,90	14,28	5,66	73,09	14,31	5,49
10	74,5	117,5/11	0,8859	1,5050	76,32	10,58	5,66	76,21	10,66	5,72
11	60,5	98,2/11	0,8286	1,4598	64,42	12,50	6,15	64,51	12,45	5,81
12	69	117/8	0,8367	1,4548	—	—	—	—	—	—
13	68	107/9,5	0,8213	1,4572	67,50	12,88	5,33	67,27	12,71	5,05
14	72,8	132—133/8,5	0,8219	1,4551	70,07	12,98	4,72	69,40	12,90	4,47
15	67	124,3/11,5	0,9252	1,5194	70,00	9,34	5,38	69,91	9,29	5,25

Aliphatic and aromatic amines reacted with trialkylborons at 170 — 200° and were smoothly converted into N-substituted dialkylboramines (III). The reaction was accompanied by the formation of saturated and olefinic hydrocarbons and hydrogen, the ratio of which depended on the nature of the starting amine (see Table 1).

$$R_3B + NH_2R' \rightarrow R_2BNHR' + RH + R_{-H} + H_2$$

(III)

R' = alkyl, C_6H_5

Mercaptans reacted with trialkylborons, even at room temperature; however, under these conditions, the process did not proceed to completion and it was necessary to heat the mixture of reagents to 140 — 150° to complete the process. As a result of the reaction we obtained 60 — 73% yields of alkyl esters of dialkylthioboric acids (IV), which were previously synthesized from trialkylborons and sulfur [9]. By the procedure indicated, together with esters of thioboric acids, the reaction gave almost exclusively the corresponding saturated hydrocarbons. Thiophenol reacted with trialkylborons at 150 — 170°.

$$R_3B + R'SH \rightarrow R_2BSR' + RH + R_{-H} + H_2$$

(IV)

R' = alkyl, C_6H_5

The reactions studied were multistep; they proceeded through the stage of the formation of a complex of the trialkylborons with oxygen, nitrogen or sulfur addends (V).

$$R_3B + \underset{\underset{H}{|}}{Y}-R' \rightarrow \underset{(V)}{R_3B \leftarrow \underset{\underset{H}{|}}{Y}-R'}$$

$Y_{\cdot} = O,\ NH,\ S$

The complex compounds (V) then underwent two types of conversion. The first of these consisted of decomposition of the complexes (V) into saturated hydrocarbons and the corresponding organoboron compounds (VI) by the scheme

$$\underset{\underset{R}{|}}{R_2B} \leftarrow \underset{\underset{H}{|}}{Y}-R' \rightarrow R_2BYR' + RH \quad (VI)$$

$Y = O,\ NH,\ S$

This process evidently proceeded through the stage of the removal of a proton from the heteroatom and cleavage of the alkyl group from the boron atom in the form of an anion.

The second direction of decomposition of the complex compounds (V) consisted of elimination of an olefinic hydrocarbon and hydrogen and the formation of compound (VI) by the scheme

$$R_3B \leftarrow \underset{\underset{H}{|}}{Y}-R' \rightarrow R_2BYR' + R_{-H} + H_2 \quad (VI)$$

$Y = O,\ NH$

This process is most clearly expressed by the reaction of trialkylborons with water, alcohols or amines. It proceeds at a high rate when there is excess trialkylboron in the reaction mixture. The effect of complex formation on the rate of the elimination reaction is shown by the thermal decomposition of tri-n-butylboron pyridinate. We found that the elimination of butylene was complete after 6 hours heating at 180° in this case, while tri-n-butylboron underwent an analogous conversion at the same temperature only after 10 days' heating [10]. It is possible that the conversion of complexes (V) by scheme (3) proceeds through the stage of dialkylborane complexes (VII), which then rapidly eliminate a molecule of hydrogen:

$$R_3B \leftarrow \underset{\underset{H}{|}}{Y}-R' \rightarrow \underset{(VII)}{R_2HB \leftarrow \underset{\underset{H}{|}}{Y}-R'} + R_{-H} \rightarrow R_2BYR' + H_2. \quad (VI)$$

The reactions we studied are simple and very convenient as preparative methods for obtaining dialkylboric acids, their esters, N-substituted dialkylboramines and esters of dialkylthioboric acids.

EXPERIMENTAL

I. Synthesis of trialkylborons. To a 4 M ether solution of n-butylmagnesium bromide (1.8 moles) was added 0.19 mole of isobutyl metaborate. The reaction mixture was boiled for 2 hours and treated with 7% hydrochloric acid. The ether and alcohol were removed in vacuum in the presence of excess water at a temperature of not more than 50°. The yield of tri-n-butylboron was 89 g (85%) and the b.p. was 85 – 86°/8 mm. Tri-n--propylboron, triisopropylboron, triisobutylboron and triisoamylboron were prepared similarly.

II. Reaction of trialkylborons with water. Into an apparatus, consisting of a three-necked flask with a reflux condenser, a thermometer and a nitrogen inlet tube, was placed 0.07 – 0.1 mole of trialkylboron. The apparatus was connected to a gasometer, the starting trialkylboron heated to 160 – 170°* and over a period of

*The reaction with triisopropylboron was carried out at 130 – 140°.

one hour, and equimolar amount of oxygen-free water was added to it. In the preparation of diisoamylboric anhydride from triisoamylboron, a trap cooled to -70° was placed between the apparatus and the gasometer. The reaction mixture was heated for a further 2 — 3 hours at 170 — 180°, then cooled to room temperature and the apparatus flushed with nitrogen. The gaseous mixture was analyzed and the liquid reaction products fractionated in vacuum.

III. Reaction of trialkylborons with alcohols. To 0.053 — 0.075 mole of tri-n-butylboron was added an equimolecular amount of alcohol or phenol and the mixture boiled until the evolution of gaseous hydrocarbons ceased. Ethyl alcohol was added to heated tri-n-butylboron in small portions so that the boiling point of the mixture was not below 100 — 115°.

IV. Reaction of trialkylborons with amines. An equimolecular mixture of trialkylborons with n-butylamine was heated at 190 — 200° for 2 — 3 hours. Heating for one and a half hours at 170° was required to complete the reaction of tri-n-propylboron with aniline.

V. Reaction of trialkylboron with mercaptans. Equimolecular amounts of trialkylborons and mercaptans were mixed at room temperature. As gas was evolved, the mixture was gradually heated to 150°. The esters of dialkylthioboric acid obtained were colorless substances with a repulsive smell, which were miscible with organic solvents and oxidized in air. The results of the experiments are presented in Table 1.

VI. Tri-n-butylboron pyridinate. The complex of tri-n-butylboron with pyridine was formed by mixing equimolecular amounts of the starting materials and had b.p. 95 — 97°/5 mm, d_4^{20} 0.8581, n_D^{20} 1.4870.

Found %: C 77.61; H 12.46; B 4.51 $C_{17}H_{32}BN$. Calculated %: C 78.16; H 12.35; B 4.14

0.03 mole of tri-n-butylboron was heated for 5.5 hours at 180 — 200°. We obtained 0.031 mole of butylene.

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THE SENSITIVITY LIMIT OF ANALYTICAL REAGENTS

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Many of the analytical reagents used at the present time make it possible to detect with certainty fractions of a microgram of the substances sought over a considerable range of dilutions [1, 2]. Nonetheless, in a series of cases such sensitivity is insufficient as is indicated by the continuous search for new reagents and the development of methods for concentrating the component sought or, and the search for analytical forms.

The sensitivity of a given reagent for this or that substance, although it also depends on a whole series of factors (nature of the solvent, reaction medium, temperature, character of analytical effect, observation method, presence of interfering substances etc.), with other conditions equal, is determined by the chemical structure of the final reaction product. It is precisely the latter which predetermines such important properties of the analytical form as solubility and depth and intensity of color [3 – 8]. The importance of these properties is due to the fact that,in practice, in an overwhelming majority of cases we deal with either precipitation reagents or colorimetric reagents. As in known, as an analytical effect, the first of these shows the appearance (or disappearance) of a colorless or colored precipitate, whose solubility determines the sensitivity. In the case of colorimetric reagents, the analytical effect is reduced to a change in the character of the color of the solution; it is clear that here the sensitivity depends on the color properties of the analytical form.

At the present time, chemical analysis has a vast arsenal of reagents, which are mainly organic and whose number continues to grow. For some ions there are already hundreds of substances, but the search for new and more sensitive or more specific reagents continues without ceasing for a day. Here, one must consider to what extent these searches are worthwhile in each separate case.

The sensitivity for direct detection of any substance sought by means of chemical reactions must have some minimal value, below which it is impossible to extend the physical and physiological rules of perception of the analytical effect. These rules have hardly been considered in textbooks and handbooks, which most often confine themselves to discussion of the interrelation between the certain detection minimum and the limiting dilution.

Obviously, if the basis of the analytical process is a noncatalytic, visual observation of a chemical reaction, for which excess reagent has been taken, then the appearance of a precipitate or a change in color of the solution will only be appreciable when the concentration of the substance sought is not less than required for the limiting dilution in the given reaction. Otherwise, the analytical effect will not be observed, although the analytical form may be present in amounts limited by its solubility product or instability constant. This state of affairs is caused by the sensitivity of the normal eye in perceiving a difference in color or the illumination of objects or surfaces compared. For example, between ideal white and absolute black surfaces one can consider theoretically an infinite number of grey surfaces, colored with so-called achromatic colors. However, in the best case, the normal eye can only distinguish between about 250 of these.

Consequently, at normal light-flux intensities we are capable of perceiving 0,4% differences in the illumination of two identical surfaces. In the case where we observe a light flux, not after reflection, but after transmission through some medium, then two equal areas examined by us will seem differently illuminated only when 0,4% of one of them is shielded.

The situation is completely analogous with the capacity of the eye for distinguishing between different colors in the visible region of the spectrum; the sensitivity of the eye has a limiting value, which varies for different colors. Let us assume that we are observing in transmitted daylight, the interaction in solution of the substance sought and a precipitation reagent with the limiting sensitivity for it; in this interaction, a colorless, completely insoluble substance is formed from colorless components.

We may detect this visually only when, as already stated, the precipitate cuts off ~0.4% of the light transmitted through the solution, i.e., when the area of the precipitate is of the order of 0.4% of the whole area considered.

The precipitate will probably not be in one piece, but will consist of a large number of separate particles; the dimensions of the latter in all three directions should be of the order of 1 μ or otherwise they will be partially by-passed by the light flux. Consequently, the apparent thickness of the precipitate, consisting of even a single layer of particles, cannot be less than 10^{-4} cm. These considerations make it possible to calculate the volume of the precipitate; the weight of the precipitate, formed in a certain volume of solution of the reacting substances, may be calculated starting from the premise that its specific gravity is close to 1. Neglecting light scattering processes, we may then calculate approximately the molar concentration of the component sought at the limiting dilution of it in a reaction with precipitation reagent of limiting sensitivity.

The dependence of the sensitivity of colorimetric reagents on the depth and intensity of the color of the analytical form has been considered in the literature several times [9 — 12]. Their limiting sensitivity may be calculated, starting from the known equation $\epsilon = D/Cl$ in which all the symbols denote characteristics of the analytical form: ϵ is the molar absorption coefficient; D is the optical density of the solution; C is the concentration of the solution in mole/liter and l is the thickness of the solution layer in centimeters.

The normal eye can always distinguish with certainty between an optically clear solution and a solution with an optical density of about 0.02. Consequently, D of a solution of an analytical form at the sensitivity limit of the type of reagents we are examining may not be less than 0.02.

If we then assume that ϵ of the analytical form equals 10^5 (in practice this value is most frequently of the order of 10^4), then we have all the data for an approximate calculation of the limiting sensitivity of colorimetric reagents at a given layer thickness of a colored solution, for example, at l = 1 cm.

Table 1 gives the sensitivity for detecting a substance (M is the molecular weight) by means of reagents of the type considered.

TABLE 1

Calculated Data for the Limiting Sensitivity of Colorimetric Reagents at a Layer Thickness of 1 cm and Precipitation Reagents

For detecting a substance	Reagent	
	colorimetric	precipitation
Minimal conc. in mole/liter	10^{-7}	10^{-6}
Detection minimum μg/ml	10^{-4}M	10^{-3}M
Limiting dilution	1 : 10^9 M	1 : 10^8 M

The figures in this table, firstly give a logical basis for the fact that with other conditions equal, precipitation reagents giving colored analytical forms are found to be more sensitive than reagents giving colorless precipitates.

Secondly, for example, we can state that it is doubtful if a precipitation reagent for lithium exists which would make it possible to detect it directly in concentrations much less than 0.05 μg/ml; this detection minimum, for example, for the uranyl ion cannot be surpassed by the use of colorimetric reagents either.

Naturally, the calculations presented are extremely approximate and they do not consider certain important factors (reaction equations, solubility of precipitates and variation in the dimensions of their particles, light scattering, stability of the analytical form etc.); however, they are sufficiently accurate for evaluation in each actual case the prospects of a search for more sensitive reagents.

These elementary calculations, in addition, indicate feasibility of developing effective methods of overcoming the insufficient sensitivity of reagents of limiting sensitivity.

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INVESTIGATION OF THE COPOLYMERIZATION OF ISOPRENE WITH PIPERYLENE AND DIISOPROPENYL

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In the present communication we give the results of work which is a development of a previous investigation of the copolymerization of divinyl and isoprene. As in the previous case we used isoprene containing the radioactive isotope C^{14}. Most of the experiments on the separate polymerization and copolymerization of isoprene, piperylene and diisopropenyl in hexane solution with butyllithium were carried out at 50° with a catalyst concentration of 0.01 mole/liter and a monomer concentration of 2 moles/liter. The procedures for the

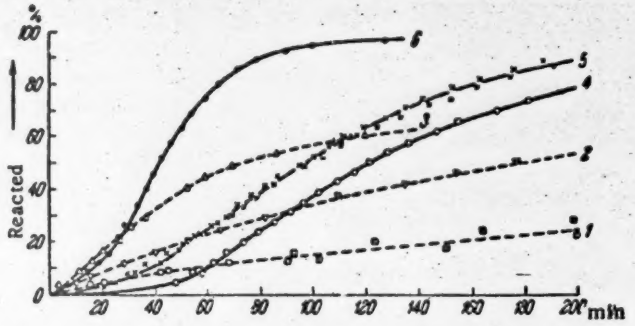

Fig. 1. Kinetic curves of the polymerization of piperylene: (1-50°, 2—60°, 3—70°) and diisopropenyl (4 and 5—70°, 6—80°), C_{mon} = 2 mole/liter, C_{cat} = 0.01 mole/liter (in the case of 5, 0.02 mole/liter and for 6, 0.03 mole/liter)

polymerization and the synthesis of isoprene labeled with C^{14} were described previously [1, 2].

In separate polymerization with butyllithium, isoprene was the most active monomer (see Fig. 2.). In the stationary period, the rate of polymerization of isoprene at a butyllithium concentration of 0.0035 mole/liter was approximately 0.1 mole/liter·min and of piperylene and diisopropenyl, 0.0035 — 0.0040 mole/liter·min at a butyllithium concentration of 0.01 mole/liter.

The course of the polymerization of piperylene differed from that of diisopropenyl in the absence of a noticeable induction period. Consequently, in the polymerization of piperylene, the rate constant of the chain generation reaction, i.e., the interaction of the monomer with the starting catalyst —butyllithium, is similar to the rate constant of the chain growth reaction, while in the case of diisopropenyl, the first constant is considerably less than the second.

Increasing the butyllithium concentration from 0.01 to 0.02 mole/liter led to a reduction in the induction period by a factor of approximately two, but the rate of the polymerization reaction of diisopropenyl in the

stationary period hardly changed. The existence of such a dependence indicates the presence of deactivation of active polymerization centers due to their interaction with each other, similar to that which occurs in the polymerization of isoprene by butyllithium [3]. It should be noted that the fall in the polymerization reaction rate of piperylene in the region above 50% conversion is considerably greater than would be expected as a result of the decrease in the monomer concentration. As yet no explanation for this phenomenon has been found.

The reaction rates of diisopropenyl and piperylene polymerization in the stationary period are approximately the same (see curves for 70° on Fig. 1).

In copolymerization, the reaction rate and the composition of the copolymers are determined by the polymerization rate of the monomers in the stationary period and therefore, it is not unexpected that the kinetic curves for the copolymerization of isoprene with diisopropenyl and piperylene practically coincide (Fig. 2, 2).

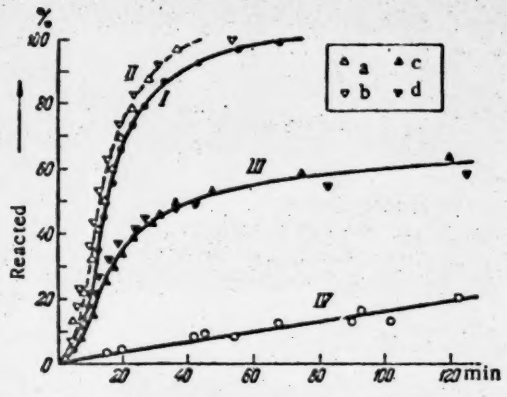

Fig. 2. Kinetic curves of separate and copolymerization at 50°: I) isoprene; II) calculated curve (amount of monomers reacting in copolymerization expressed relative to the initial amount of isoprene): a) isoprene — piperylene, b) isoprene —diisopropenyl; III: c) isoprene — piperylene (1 : 1), d) isoprene — diisopropenyl (1 : 1), IV) piperylene

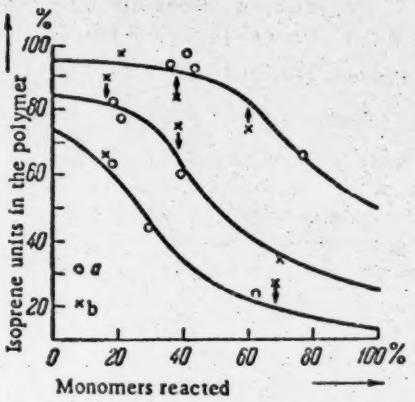

Fig. 3. Calculated integral curves of copolymer composition for the systems isoprene — piperylene and isoprene — diisopropenyl at 50° (a, b — exp. points); $\alpha = 17$, $\beta = 0.06$

If the amount of monomers reacting in copolymerization is expressed in percents of the isoprene taken, then the kinetic curve lies close to that for the separate polymerization of isoprene (curves 1a and 1 in Fig. 2). A certain displacement of the curve is connected with the somewhat higher reaction rate due to the increased catalyst concentration (0.01 instead of 0.0035 mole/liter) in experiments on copolymerization and the slight distortion of the results because of the participation of piperylene or diisopropenyl in the chain growth reaction, especially during the period of isoprene depletion. Thus, in the initial period, the reaction rate of copolymerization corresponds to the reaction rate of separate polymerization of isoprene and after exhaustion of the isoprene, to the rate of separate polymerization of the second monomer.

As has already been mentioned, diisopropenyl and piperylene differ in the rate of chain generation. In their copolymerization with isoprene, this difference is absent and the kinetic curves coincide; consequently the more active monomer, isoprene, is responsible for the reaction rate of chain generation.

Usually, during the growth of copolymer chains, the participation of each monomer is proportional to its concentration and relative activity and depends greatly on the activity of the polymerization centers at the ends of the polymer chains formed by the given monomer. Judging by the copolymerization kinetics, in the case considered the rate of copolymer chain growth does not depend on the form of the monomeric unit forming the polymerization center. In other words, the activity of the polymerization center is not affected by the monomer forming it, i.e., $K_{11} = K_{21}$ and $K_{22} = K_{12}$. Therefore, for the case of copolymerization of isoprene with piperylene or diisopropenyl it is possible to use the equation proposed by Wall [4]:

$$\lg \frac{A}{A_0} = \alpha \lg \frac{B}{B_0} \quad \text{or} \quad \frac{A}{A_0} = \left(\frac{B}{B_0}\right)^{\alpha},$$

where

$$\alpha = \frac{K_{11}}{K_{12}}; \quad \beta = \frac{1}{\alpha} = \frac{K_{12}}{K_{11}}.$$

For three ratios of isoprene to second monomer (1 : 1, 1 : 3 and 1 : 6.4), the experimental points lie about the copolymerization curves constructed for $\alpha = 17 \pm 5$ and, correspondingly, $\beta = 0.06 \pm 0.02$ (see Fig. 3). In the copolymerization of piperylene, practically all the points lie within the limits of experimental error, but in the case of diisopropenyl their scatter was found to be considerably greater.

TABLE 1

Results of Experiments on the Copolymerization of Isoprene and Piperylene in Hexane at Several Temperatures and with the Addition of Diethyl Ether at 60°

Exp. No.	Temp., °C	Ether content of solvent, %	Extent of conversion, %	Isoprene content, mole %		Max. reaction rate, mole/liter. min.	α_{calc}
				in initial mixture	in polymer		
24	50	0	19.4	19.8	67.7	0.026	13.6
21	60	0	20.6	20.2	65.7	0.066	12.0
22	70	0	21.2	20.0	62.8	0.158	10.5
25	70	0	24.2	20.0	64.4		13.3
23	80	0	28.0	20.0	62.8	0.182	15.0
26	30	0	28.6	20.6	56.6		9.1
28	60	5	26.4	20.0	54.5	0.116	7.8
27	60	10	27.9	20.0	44.7	0.172	5.0
29	60	20	34.9	20.0	43.4	0.170	4.9

The value of the copolymerization constant hardly depends on temperature (see Table 1, exps. No. 21 - - 26). Consequently, the activation energy of the chain growth reaction due to isoprene does not differ essentially from that for piperylene. Meanwhile, the rate constants of these reactions differ by a factor of approximately 20. Hence, the lower activity of piperylene is due exclusively to the steric factor, the presence of steric hindrance in comparison with isoprene.

The rate of polymerization and copolymerization of diethylene hydrocarbons by butyllithium is considerably increased in the presence of even small amounts of ethers and other complex-forming compounds. The same phenomenon was observed in the copolymerization of isoprene and piperylene (Table 1, exps. No. 21 and 27 - - 29). With an increase in the diethyl ether concentration, the copolymerization rate in the initial period increases and tends to a limit in the concentration region equal to approximately 10% of ether in the solvent. The maximum reaction rate exceeds that in the pure solvent by a factor of approximately three. With an increase in the ether concentration, the composition of the copolymer also changes. The content of isoprene units falls from 63 — 68% in a copolymer obtained in pure solvent to 43 — 45% and the corresponding copolymerization constant α falls to 5. Ether only has substantial effect on the rate and direction of the copolymerization reaction at relatively high concentration of more than 100-fold excess over the concentration of butyllithium. The results obtained give grounds for proposing that the active polymerization center in an ether medium is an unstable complex, containing two or more molecules of diethyl ether:

$$R \cdot Li\,[O(C_2H_5)_2]_2 \quad \text{or} \quad R \cdot Li\,[O(C_2H_5)_2]_3.$$

Such a complex active polymerization center leads to a relatively great acceleration of the chain growth reaction due to a piperylene (approximately 2.5 times greater than due to isoprene).

Hence, though in the copolymerization of isoprene with divinyl there is "reversal" of activity and it is impossible to predict the composition of the copolymer formed on the basis of data on separate polymerization; in the cases considered here the relative activity of the monomers in separate and copolymerization is retained and may be expressed by the series: isoprene" >> piperylene " ≥ diisopropenyl. This difference in activities is caused only by steric factors; it does not change with an increase in temperature and decreases substantially if the polymerization reaction is performed in a mixed solvent: hexane + diethyl ether.

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ELECTRONIC NATURE OF SUBSTITUENTS IN DIENE AND DIENOPHILE AND THE STRUCTURAL DIRECTION OF DIENE SYNTHESIS*

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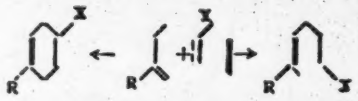
(Presented by Academician B. A. Kazanskii March 3, 1959)

In the diene condensation of unsymmetrically substituted dienes with unsymmetrical dienophiles, of the two possible structural isomers, one particular one is formed predominantly. This structural selectivity is undoubtedly connected with the mechanism of diene synthesis and therefore its study may be one method of establishing the mechanism of this important reaction.

To study the structural direction, we chose as the dienophiles acrylic acids containing the electron-acceptor carboxyl group and styrene with an electron-donor phenyl group; these dienophiles were subjected to diene condensation with both 1-substituted and 2-substituted dienes.

In the case of 2-substituted butadienes, the composition of the adducts was established by various methods depending on the type of substituent in the diene.



R = CH_3; C_6H_5; OCH_3; Cl. X = COOH; C_6H_5.

By dehydrogenation and oxidation, adducts with isoprene were converted into the corresponding aromatic acids, whose ratio indicated the composition of the starting mixture. In the case of 2-phenylbutadiene, the isomeric adducts could be separated by fractional crystallization. Finally, adducts of 2-methoxybutadiene and chloroprene were converted by acid hydrolysis into the corresponding keto compounds, which were separated by crystallization and chromatography on aluminum oxide. The results obtained are presented in Table 1.

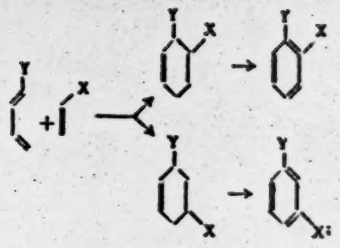
The data in Table 1 show that despite the difference in their electronic properties, the substituents studied do not have sharply expressed differences as regards directing effect in diene condensations. Nonetheless, the ratio of the isomers obtained depended to a definite extent on the nature of the substituents and in terms of directing effect, the substituents in the diene may be arranged in the following order:

$$Cl > CH_3O > C_6H_5 > CH_3$$

According to our data, a phenyl substituent in the dienophile is a stronger para-director than a carboxyl.

The structural direction of diene synthesis for 1-substituted dienes was also studied for all possible combinations of phenyl and carboxyl substituents in the two components. The condensations were carried out by heating a mixture of diene and dienophile at 150° for 3 — 50 hours.

* This work is a continuation of investigations carried out under the direction of Academician I. N. Nazarov.



X = COOH; C_6H_5. Y = COOH; C_6H_5.

To prove the structure, the adducts obtained were dehydrogenated into the corresponding aromatic compounds, which were separable by crystallization and chromatography on aluminum oxide. The results obtained are presented in Table 2.

From the point of view of the ionic mechanism of diene synthesis [1, 2], where the polarities of the ends of the molecules of diene and dienophile are not the same (No. 1 and 4 in Table 2), we should obtain predominantly the ortho-isomer and where the polarities are the same (No. 2 and 3 in Table 2), the meta-isomer. However, we showed that in all cases the ortho-isomer predominated in the mixture of adducts obtained and this apparently excludes the determining role of the molecules' polarity in the structural direction of diene synthesis.

TABLE 1

Condensation of 2-Substituted Butadienes With Unsymmetrical Dienophiles

R	X	Reaction conditions	Yield of adducts, %	Constants of adducts		Ratio of para and meta isomers
				b.p., (°C/mm)	n_D^{20}	
CH_3	COOH	200° 2 hr.	80	140—145/15	•	1,9:1
C_6H_5	$COOCH_3$	150° 5 hr.	73	165—166/6	•	4,5:1
CH_3O	COOH	150° 10 hr.	72	151—155/12	1,4722	8:1
Cl	COOH	150° 5 hr.	83	162—165/17	•	9,3:1
CH_3	C_6H_5	200° 10 hr.	31	120—122/20	1,5356	3,5:1
C_6H_5	C_6H_5	150° 50 hr.	54	210—215/10	•	only para
CH_3O	C_6H_5	150° 10 hr.	59	140—145/12	1,5170	12:1
Cl	C_6H_5	150° 12 hr.	20	110—114/8	1,5548	14,3:1

• The adduct was partly crystalline.

TABLE 2

Condensation of 1-Substituted Butadienes With Unsymmetrical Dienophiles

No.	Y	X	Yield of adducts, %	Constants of adducts		Ratio of isomers	
				b.p., (°C/mm)	n_D^{20}	ortho : : meta	ortho-trans / ortho-cis
1	C_6H_5	$COOCH_3$	61	144—149/5	1,5372	39:1	8:1
2	C_6H_5	C_6H_5	33	190—198/10	1,5912	8,1:1	—
3	COOH	COOH	86	170—175/35	•	8,8:1	8,6:1
4	COOH	C_6H_5	58	220—225/25	•	5,7:1	17:1

• The adduct was partly crystalline.

In addition, in the case of 1-substituted dienes, the nature of the substituents has a definite effect on the ratio of structural isomers. Thus, in the presence of an electron-donor substituent in the diene and an electron-

-acceptor substituent in the dienophile (No. 1 in Table 2), the meta-isomer represents only 2 — 3% of the mixture. In the case of identical polarities of the substituents (No. 2 and 3 in Table 2), the amount of meta-isomer increases to 10 — 11%. Finally, with an electron-acceptor substituent in the diene and an electron-donor substituent in the dienophile (No. 4 in Table 2), the structural selectivity is even weaker and the amount of the meta-isomer reaches about 15%.

Thus, on the basis of the results we obtained, we may conclude that the transition from electron-donor to electron-acceptor substituents in the diene or dienophile does not produce a reversal of structural direction as should be the case with an ionic mechanism for diene synthesis [1, 2]. Therefore, the ionic mechanism should be rejected as it does not explain one of the basic rules of the reaction. The mechanism of diene synthesis through kinetically independent free radicals with an open chain [3, 4], apparently, is also inadmissible, since it is incompatible with the presence of steric selectivity in the reaction [5] and the fact [6, 7] that free radicals are not formed in retrodiene decomposition. Apparently, the most probable mechanism for diene synthesis is that involving homolytic regrouping of electrons within a cyclic transition complex, which is stereochemically similar to the adduct.

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δ - LACTONES. 3-BROMOPYRONES-2

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As is known from literature data, the bromination of pyrones-2 leads to the formation of 3-bromo substituted pyrones [1 — 4].

In the present work we prepared a series of 3-bromopyrones-2 (not described in the literature) from 5, 6-dialkylpyrones-2 and 5, 6-cycloalkanopyrones-2, synthesized from the corresponding δ-enol lactone dibromides by a method we developed [5, 6]:

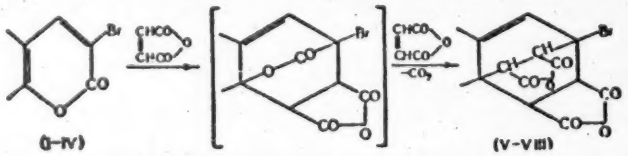
(I) R=CH₃; (II) R=C₂H₅

(III) n=1; (IV) n=2

The yield of 3-bromopyrones-2 was 28 — 56%. 3-Bromo-5, 6-dimethylpyrone-2 (I), 3-bromo-5-ethyl-6-methylpyrone-2 (II), 3-bromo-5, 6-cyclopentanopyrone-2 (III) and 3-bromo-5, 6-cyclohexanopyrone-2 (IV) were synthesized.

Then, for the first time a study was made of the behavior of 3-bromopyrones-2 in diene synthesis (in a reaction with maleic anhydride).

It was found that like pyrones-2, 3-bromopyrones-2 readily underwent diene synthesis with maleic anhydride, liberating carbon dioxide and forming crystalline double adducts (V — VIII; the yield was 50 — 80%), corresponding to the addition of two molecules of maleic anhydride to a molecule of bromopyrone:



(I–IV) (V–VIII)

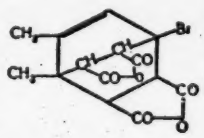
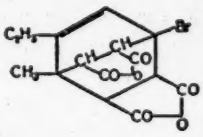
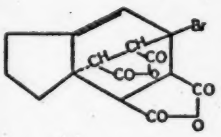
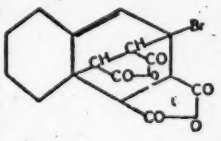
TABLE 1

3-Bromopyrones-2

Formula No.	Name	M.p. °C	Yield %	Found %		Formula	Calculated %	
				C	H		C	H
I	3-Bromo-5, 6-dimethylpyrone-2	97—98	53	41,84 41,68	3,84 3,70	$C_7H_7O_2Br$	41,42	3,48
II	3-Bromo-5-ethyl-6-methylpyrone-2	66—67 (from aqueous alcohol)	38	44,63 44,67	4,25 4,40	$C_8H_9O_2Br$	44,26	4,18
III	3-Bromo-5, 6-cyclopentanopyrone-2	140—141	28	44,99 45,08	3,38 3,47	$C_8H_7O_2Br$	44,70	3,28
IV	3-Bromo-5, 6-cyclohexanopyrone-2	131—132	56	47,12 47,32	3,93 4,20	$C_9H_9O_2Br$	47,19	3,96

TABLE 2

Double Adducts of 3-Bromopyrones-2 With Maleic Anhydride

Formula No.	Formula	M.p.,°C	Yield %	Found %		Formula	Calculated %	
				C	H		C	H
V		289—290	71	47,68 47,72	3,22 3,38	$C_{14}H_{11}O_5Br$	47,35	3,12
VI		305—306	82	48,68 48,80	3,67 3,69	$C_{15}H_{13}O_5Br$	48,78	3,56
VII		318—319	60	48,85 49,01	3,03 3,02	$C_{15}H_{11}O_5Br$	49,06	3,00
VIII		282—283 (from acetonitrile)	51	50,26 50,37	3,55 3,62	$C_{15}H_{13}O_5Br$	50,40	3,44

EXPERIMENTAL

Bromination of pyrones-2. To a solution of 0.05 mole of pyrone-2 in 30 ml of absolute ether was added 0.06 mole of bromine with water cooling and the reaction mixture left over night. After evaporation of the solvent and the excess bromine, the residue crystallized. The constants, yields and analysis data of the 3-bromopyrones-2 obtained, after their recrystallization from alcohol, are presented in Table 1.

Preparation of adducts of 3-bromopyrones-2 with maleic anhydride. A solution of 0.004 mole of the 3-bromopyrone-2 and 0.008 mole of maleic anhydride in 4 ml of xylene was boiled for two hours; evolution of carbon dioxide was observed. The precipitated crystalline adduct was purified by solution in ethyl acetate and subsequent precipitation with petroleum ether.

The melting points, yields and analysis of the adducts obtained (V — VIII) are presented in Table 2.

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ON THE PARAMAGNETIC RESONANCE OF α, α-DIPHENYL-β-PICRYLHYDRAZYL PREPARED FROM DIFFERENT SOLVENTS

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Data cited by different authors on the width of the paramagnetic resonance lines of α, α-diphenyl-β-picrylhydrazyl (DPPH) vary within wide limits (from ~1 to ~6 oersteds). Such a great difference cannot be explained merely by the effect of adsorbed atmospheric oxygen, as was proposed in reference [1].* In order to clear up this question, we undertook a series of measurements proposed by one of us (A. E. Arbuzov) in which paramagnetic resonance measurements were made with samples of DPPH prepared using different solvents.

The method used for the preparation of the DPPH has been described in reference [3]. In contrast to the method of Goldschmidt [4], the DPPH samples were obtained from the solutions not by precipitation with ether, but by evaporation of the solvent under vacuum at temperatures as low as possible, which only in individual cases amounted to 40-50 deg C. The following solvents were used: benzene, toluene, xylene (a mixture of the isomers), pyridine, bromoform, carbon tetrachloride, chloroform, and carbon disulfide.

The measurements were carried out at frequencies of ν_1 = 300 megacycles and ν_2 = 9400 megacycles by the method described in reference [5]. They were made at 295 and 90 deg K at the frequency ν_1 and at 295 deg K at the frequency ν_2. Below are presented the values of the widths of the paramagnetic absorption lines $(\Delta H)_{\frac{1}{2}}$. The data related to finely crystalline samples placed in sealed tubes from which the air was preliminarily pumped to a high vacuum. As may be seen, the nature of the solvent had a substantial effect on the width of the lines. Hence, it is natural to conclude that molecules of the solvent enter into the crystal lattice of the DPPH. This has already been established for some cases [6-9]. However, both from a consideration of the literature data and from our own analytical results it follows that in not one single case is there any guarantee that the experimenter was dealing with chemically pure individuals.

The results cited in Table 1 show that our solvents can be divided into two groups with respect to their effect on the width of the lines: ring compounds and compounds not containing rings.

A narrowing of the absorption lines upon increase in frequency and when the sample was cooled was observed with DPPH samples containing molecules of cyclic solvent in the crystal lattice. On the other hand, a broadening of the lines with an increase in frequency and with a decrease in temperature occurred in samples of DPPH containing acyclic solvent molecules.

The slight width of the lines indicates a very high exchange in all of the DPPH samples investigated. This is confirmed also by the ratio of the fourth moment to the second calculated from our data. Thus, for Sample 1 at 295 deg, $M_4/M_2 = 1.36$, and for the same sample at 90 deg K it is 1.39; for Sample 7 at 295 deg K it is 1.44.

Generally speaking, the width of the lines was greater for the first group (1-4) than for the second (5-8). This is apparently connected with a difference in their crystal structures, which leads to a larger exchange integral for samples of the second group than for those of the first group.

* The effect of atmospheric oxygen on the width of the paramagnetic resonance lines of DPPH was later noted in reference [2] also.

The slight narrowing of the lines with an increase in frequency observed with samples of the first group is in agreement with the theory of Kubo and Tomita [11] for purely isotropic exchange, and it results by reason of the disappearance in strong magnetic fields H of nonsecular broadening of the lines, the "10/3" effect. The increase in ΔH when these samples are heated can be understood on the basis of this same theory as being the consequence of the dependence of nonsecular broadening on correlation time: the latter can only decrease with an increase in temperature, which must also broaden the line.

The broadening of the lines with an increase in the frequency ν, observed for samples of the second group is apparently connected with their greater g-factor anisotropy as compared to that of the samples of the first group. This effect was previously noted in reference [12].

Broadening of the lines with cooling was first found for DPPH by Singer [13], and was ascribed to a weakening of intramolecular motion; our experiments show that it occurs only with variants of the second group. In these samples, the presence of greater g-factor anisotropy apparently makes the contribution of nonsecular broadening in ΔH less substantial, as a consequence of which the effect of temperature on ΔH depends mainly on other causes not connected with exchange, most probably that pointed out by Singer.

To sum up, it can be said that the samples of the first group, which contain cyclic-type solvent molecules in the crystal lattice, are, in spite of the great breadth of the lines, apparently more magnetically isotropic than the samples of the second group. All of the considerations presented here are very preliminary. Final clarification of the observed dependence $\Delta H(\nu, T)$ requires investigation of the paramagnetic resonance in single crystals of all of the varieties of DPPH and the obtaining of detailed information on the structure of their crystal lattices.

TABLE 1

Breadth of Paramagnetic Absorption Lines $(\Delta H)_{\frac{1}{2}}$ of Various Samples of DPPH (in oersteds)

Expt. No.	Solvent	At $T=295°$ K	At $T=90°$ K	At $T=20°$ K
1	Benzene	6,8	4,6	4,7
2	Toluene	2,9	2,6	2,6
3	Xylene (mixture)	2,5	2,2	2,3
4	Pyridine	5,3	5,0	5,0
5	Bromoform	2,2	2,5	2,5
6	Carbon Tetrachloride	1,9	2,7	2,3
7	Chloroform	1,7	2,1	2,0
8	Carbon disulfide	1,3	1,3	1,5

The two groups of DPPH samples displayed, at the same state of subdivision, a difference in the effect of atmospheric oxygen on line width. In the case of Samples 1-4, oxygen had practically no effect on ΔH at room temperature, while with Samples 5-8 an increase in the air pressure from $5 \cdot 10^{-5}$ to 1500 mm Hg at room temperature led to a uniform broadening of the lines. It was particularly great for DPPH obtained from carbon disulfide solution, which, in the absence of oxygen, gave the narrowest line of all. Thus, for our Sample 8, at an air pressure of 760 mm and a temperature of 295 deg K ΔH increased to 4.5 oersteds.

The phenomenon of line broadening by oxygen is fundamentally reversible in character; however, as a result of oxidation by adsorbed oxygen a certain part of the paramagnetic centers are apparently lost, since paramagnetic resonance disappeared practically completely in very finely divided samples which were allowed to stand in air for a sufficiently long time.

Experiments on saturation of the lines, which were carried out at the low frequency ν_1, showed that not only line broadening, but also a reduction in the spin-lattice relaxation time, T_1, occurred as a result of the adsorption of oxygen.

Finally, we undertook some interesting experiments on the replacement of one solvent by another in DPPH crystals. It was found that crystals obtained from chloroform solution gave, after recrystallization from benzene,

broad paramagnetic resonance lines which conformed completely to those observed with benzene Sample 1; hence, it follows that an overwhelming part of the chloroform was replaced by benzene. On the contrary, samples obtained from benzene solution and recrystallized from chloroform completely retained the line of the benzene sample. Thus, the affinity of benzene for DPPH is apparently greater than that of chloroform.

The sample obtained from carbon disulfide solution and recrystallized from benzene gave a line corresponding to the benzene sample, and the sample obtained from benzene solution and recrystallized from carbon disulfide gave a line corresponding to the carbon disulfide sample. Therefore, the affinities of these two solvents for DPPH must be of the same order, and the result of an experiment obviously depends on the presence of an excess of one solvent or the other.

In conclusion, we consider it necessary to point out that the use of DPPH as a standard in the determination of the number of paramagnetic centers in different substances requires great care. It is obviously necessary to agree that the DPPH preparation to be used as a standard in the determination of the number of paramagnetic centers is to be prepared using a specific solvent, benzene, for example, under conditions strictly specified for the entire synthesis cycle.

When the synthesis of the DPPH is carried out using other solvents, all details of the experiment (amount of solvent, temperature, etc.) should be given; otherwise, an experimenter will obtain diverse data.

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HYDROGENATION OF FURFURYL ALCOHOL OVER SKELETAL NICKEL CATALYST

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D. V. Sokol'skii

In connection with the great practical value of furan compounds [1], the catalytic hydrogenation of such compounds has been studied by a whole series of authors. It has been shown that the course of the hydrogenation and the final products depend on the experimental conditions and the nature of the catalyst. At ordinary temperature and pressure, the hydrogenation proceeds stepwise or directly to the tetrahydrofuran compounds; under vigorous conditions, rupture of the furan ring takes place, and the hydrogenolysis ends with the formation of alcohols, phenols, or saturated hydrocarbons [2-5].

TABLE 1

Temp. °C	Medium		96% C_2H_5OH
	0.1 *N* NaOH	H_2O	
	Reaction rate in ml H_2/min.		
8	2,6	4,0	4,3
20	3,6	4,6	7,6
40	4,6	5,6	8,8
60	4,2	5,6	7,6
Activation energy in cal./mole	3380	5900	6700

Nickel catalysts, particularly skeletal nickel, reduced the double bonds of the ring [6, 7], while copper and palladium catalysts reduced functional groups in side chains without hydrogenation of the ring [8].

The aim of the present work was a kinetic and potentiometric [9] investigation of the hydrogenation of furfuryl alcohol over skeletal nickel catalyst to determine the dependence on temperature (8, 20, 40 and 60 deg) and on the solvent (0.1 N NaOH, water, and 96% C_2H_5OH).

The skeletal nickel was prepared by the usual method, washed under conditions excluding contact with air, and, prior to an experiment, saturated with hydrogen in a bomb containing 15 ml of solvent until the potential of the reversible hydrogen electrode was reached.

Under our conditions, furfuryl alcohol added two moles of hydrogen, thereby being hydrogenated to tetrahydrofurfuryl alcohol; the reaction rate was proportional to the amount of catalyst, and, during the first half of the hydrogenation, the rate did not depend on the weight of the alcohol. Figure 1 and Table 1 present the results of the hydrogenation of 0.15 ml of furfuryl alcohol in the presence of 0.31 g of skeletal nickel at different temperatures.

The hydrogenation rate was greatest in ethyl alcohol; the addition of hydrogen proceeded somewhat more slowly in water, and the lowest reaction rate was observed in the base. An increase in the temperature accelerated the reaction.

Like the rate, the change in the potential of the catalyst during the course of the process depended on the medium; the change was the least in the base (56-36 mv at different temperatures), was greater in water (80-120 mv), and was the greatest in alcohol (130-190 mv).

The reduction of the furfuryl alcohol proceeded on the surface of the nickel, which was substantially filled with hydrogen, since the over-all decrease in potential did not exceed 0.2 v. The dependence of the reaction rate on the absolute potential decrease in the different media permitted the conclusion that the hydrogenation process

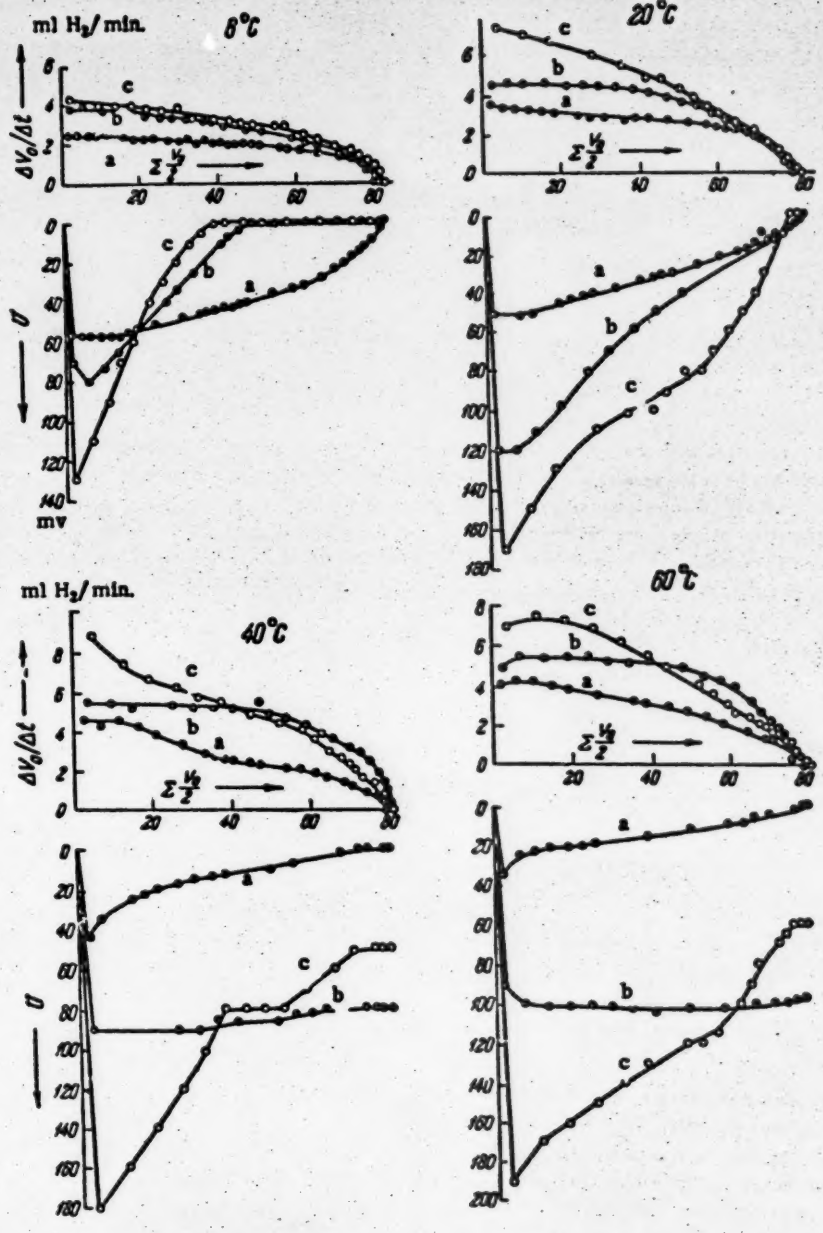

Fig. 1. The effect of the solvent and of temperature on the hydrogenation of furfuryl alcohol in the presence of skeletal nickel catalyst; a) 0.1 N NaOH; b) H_2O; c) 96% C_2H_5OH. 1) Experiments in basic medium; 2) in water; 3) in alcohol. $\Delta V_s/\Delta t$ reaction rate; $\sum \frac{V_s}{2}$ – half-sums of the volumes of absorbed hydrogen for two successive measurements; U – catalyst potential relative to the reversible hydrogen electrode in the given solution.

TABLE 2

Expt. No.	Medium					
	0.1 N NaOH		H_2O		90% C_2H_5OH	
	rate in ml/min	% change	rate in ml/min	% change	rate in ml/min	% change
I Hydrogenation	2,8		4,4		5,6	
II Hydrogenation	2,4	14,3	3,6	18,2	3,2	42,8
III Hydrogenation	2,2	21,4	3,0	31,8	2,0	64,2

is here controlled by the rate of activation of the furfuryl alcohol. Indeed, the more the catalyst potential is removed from that of the reversible hydrogen electrode, the more the catalyst surface is freed from adsorbed hydrogen, the greater the number of centers which are exposed for activation of the multiple bond, and the higher the reaction rate.

From the course of the potential curve, it is possible to estimate the rate of restoration of hydrogen on the surface of the skeletal nickel during the reaction. At 8 and 20 deg, this process proceeds significantly more rapidly in water or alcohol than in basic solution. However, in these same solvents the catalyst is more temperature-sensitive. At 40 and 60 deg, the catalyst potential does not return to that of the reversible hydrogen electrode; this may possibly be explained by activated adsorption of the functional oxygen of the furan ring, which proceeds more readily at elevated temperature.

The activation energy calculated from the kinetic data also depends on the medium and the catalyst potential, and is in good agreement with the previously proposed relationship between potential decrease, the degree of filling of the surface by hydrogen, and the activation energy [10].

The solvent in which the hydrogenation of furfuryl alcohol is carried out has a strong influence on the constancy of catalyst activity in a series of successive experiments using the same portion of skeletal nickel. This is explained by the the effect of the medium on the adsorption of reaction products, and this effect can be estimated from the ratio of the adsorption coefficients of furfuryl alcohol, B_1, and of tetrahydrofurfuryl alcohol, B_2; this ratio is found from the Langmuir equations constructed on the basis of the data of Table 2 for the first and second experiments, the values for the time when the hydrogenation had proceeded to the extent of 25% being taken

$$V_1 = K\frac{B_1C_1}{B_1C_1 + B_2C_2},$$

$$V_2 = K\frac{B_1C_1}{B_1C_1 + B_2C_2}.$$

Here, C_1 is the initial concentration of the furfuryl alcohol, C_2 and C_3 are the concentrations of furfuryl alcohol in the first and second experiments. These concentrations are expressed in terms of the volumes of hydrogen required for reduction of the given amount of alcohol.

The ratio B_1/B_2 shows that in an alcohol medium the furfuryl alcohol is adsorbed to the same extent as its reduction product; the latter, therefore, strongly reduces the catalyst activity. In water and in the basic medium, the adsorption of tetrahydrofurfuryl alcohol is less than the adsorption of the starting material by factors of 3 and 7, respectively; therefore, the activity of the skeletal nickel is more stable in these cases.

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THE ACTION OF HYDROGEN PEROXIDE ON TROPYLIUM SALTS
A NEW CONTRACTION REACTION OF THE SEVEN-MEMBERED RING

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The literature describes a number of examples of the rearrangement of tropone and tropolone derivatives under the influence of cationic reagents [1]. Benzene derivatives with the same number of carbon atoms as the original compound are formed in all of these cases. Tropylium salts undergo an analogous conversion. They are converted to benzaldehyde by the action of oxidizing agents – chromic acid, silver oxide [2], and chloroplatinic acid [3].

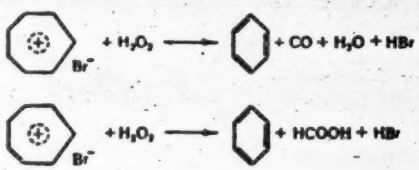
TABLE 1

Initial substance	Amount in moles	Amount in % C_7H_7Br
$C_7H_7^+Br^-$	0,0780	100%
H_2O_2	0,0780	100%
C_6H_6	0,0644	82,5%
CO	0,0393	50,4%
HCOOH	0,0390	50,0%
C_6H_5CHO		(~1,0%)
C_6H_5OH		(~0,1%)

We found that the interaction of tropylium salts with hydrogen peroxide leads to contraction of the seven-membered ring, the reaction proceeding in a direction different from those indicated above.

A rapid exothermic reaction occurs when solutions of equimolar amounts of the tropylium salt and hydrogen perioxide are mixed. The major products of this reaction are benzene, carbon monoxide, formic acid, and hydrogen bromide (see Table 1). In addition, very small amounts of benzaldehyde and phenol are formed.

The reaction thus proceeds mainly in two directions:



We studied the kinetics of the first of these reactions (accompanied by the evolution of CO). It was found that the reaction proceeds at a high rate and obeys a second-order equation with a rate constant (at 20.05 deg, in aqueous solution) of $1.04 (\pm 0.03) \cdot 10^1$ liter $mole^{-1} \cdot minute^{-1}$. A significant increase in the acidity of the medium (reaction carried out in the 1 N solution of sulfuric acid) only insignficantly decreased the reaction rate (rate constant $0.79 \cdot 10^1$ at 20 deg). The apparent activation energy in the temperature interval 20-50 deg (see Figure 1) was 10.5 kcal./mole, which is significantly lower than for typical organic reactions; the logarithm of the preexponential factor was 8.89.

The reaction of tropylium salts with hydrogen peroxide is probably not a radical reaction. This is apparent from the fact that the addition to the sulfuric acid solution of tropylium salts of equimolar amounts of iron sulfate (which promotes the radical decomposition of hydrogen peroxide and organic peroxides) not only does not

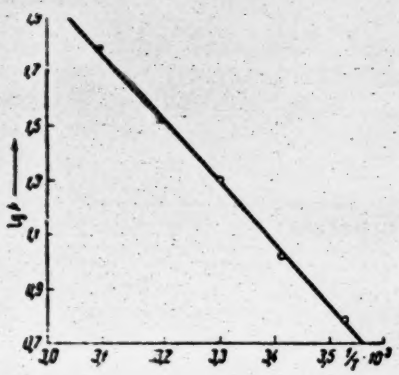
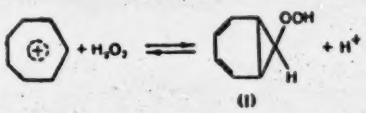


Fig. 1. Dependence of reaction-rate constant on temperature.

accelerate, but appreciably inhibits the reaction with hydrogen peroxide. The reaction rate drops by a factor of 2 to 3, and a considerable excess of hydrogen peroxide is required to force the reaction to completion.

It may be proposed on the basis of these data that the first, bimolecular stage of the reaction proceeds by the interaction of a tropylium ion with hydrogen peroxide to form the unstable hydroperoxide (I).



(I)

That the tropylium ion (and not the undissociated salt) takes part in the reaction is confirmed by the fact that substitution of tropylium perchlorate for the bromide does not change in the course of the reaction. Moreover, the reaction ceases completely in weakly alkaline media, i.e., under conditions such that the concentration of the tropylium ion is sharply decreased as a result of the reaction $C_7H_7^+ + OH^- \rightarrow C_7H_7OH$. A transfer from aqueous to alcoholic solution accelerates the reaction by an order of magnitude, and this may possibly be connected with the lower solvation of the tropylium ion.

It is possible that the hydroperoxide I either decomposes directly into the reaction products or that it is first converted to cation II by the usual mechanism of ionic hydroperoxide decomposition, and the latter undergoes cleavage to benzene and the HCO^+:

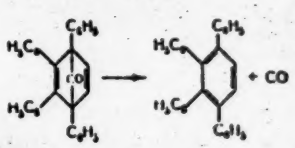
(II)

$$HC\overset{+}{=}O \longrightarrow H^+ + CO; \quad HC\overset{+}{=}O + H_2O \longrightarrow HCOOH + H^+$$

The favorable energetics of the formation of the aromatic system of benzene would promote a conversion of this type.

It would also be possible to propose that the reaction proceeds through the intermediate formation of tropone. However, tropone does not decompose to benzene and CO, and special experiments showed that it does not react with hydrogen peroxide under those conditions under which tropylium salts react. For the same reasons, the reaction does not proceed through the intermediate formation of benzaldehyde.

Thus, the ring contraction reaction studied in the present work is distinguished from other analogous reactions (for example, ring contraction in tropolones or in derivatives of cyclooctatetraene) in that it proceeds with the simultaneous rupture of two carbon – carbon bonds and with the formation of an unsubstituted benzene ring. In this respect, it can be compared to 1, 4-elimination reactions in certain bicyclic systems [5], for example:



EXPERIMENTAL

Reaction of tropylium bromide with hydrogen peroxide. A three-necked flask, fitted with a stirrer, a dropping funnel, and a reflux condenser (the upper end of which was connected to a buret for collecting the evolved gas), was purged with nitrogen, and to the flask was charged a solution of 13.34 g (0.0780 mole) of tropylium bromide in 100 ml of water. 5% hydrogen peroxide was then added while the flask was cooled with cold water. After an equivalent amount of hydrogen peroxide (~53 ml) had been added, the solution did not contain tropylium bromide (negative test with chloroplatinic acid). Stirring was continued for another 30 minutes, and the reaction mixture was then extracted with n-octane (which had first been distilled in a column). The investigation of the aqueous solution (A) is described below.

The organic extract was washed with water, a 10% solution of NaOH, and again with water, dried with magnesium sulfate, and distilled in a column (of 10 theoretical plates efficiency). 4.90 g of benzene was obtained with a b.p. of 79.6-80.1 deg/ 746 mm, n_D^{20} 1.5005.

Found %: C 92.14; 92.12; H 7.71; 7.81 C_6H_6. Calculated %: C 92.21; H 7.74

The intermediate fraction (0.95 g), b.p. 80.1-123 deg, n_D^{20} 1.4123, contained another 0.12 g of benzene (determined refractiometrically and calculated on the basis of a binary mixture of benzene and n-octane). The over-all yield of benzene was 5.02 g (82.5%).

The benzene was identified by its ultraviolet spectrum and by nitration (with a mixture of sulfuric and nitric acids) to nitrobenzene, which was then converted to aniline by reduction with zinc dust and HCl. The resulting aniline was converted to benzanilide, m.p. 160-161 deg; literature value, m.p. 162 deg; a mixture with a known sample showed no depression of the melting point.

The aqueous solution (A) was steam distilled. The distillate contained 0.0390 mole of formic acid (determined by titration of an aliquot portion with potassium permanganate). The formic acid in part of the distillate was identified by conversion to the p-bromophenacyl ester, m.p. 141-142 deg; literature data, m.p. 142 deg; a mixture with a known sample showed no depression of the melting point.

The 1000 ml of gas (at 746 mm and 19.6 deg; collected over saturated NaCl solution) evolved during the reaction contained 98.6% CO and 1.4% O_2; the latter was probably formed by partial decomposition of the hydrogen peroxide.

Reaction of tropylium perchlorate with hydrogen peroxide. To 9.8 g (0.05 mole) of tropylium perchlorate was gradually added, with cooling, 8 ml of 25% hydrogen peroxide in 30 ml of water; the reaction mixture was extracted with ether. The ether extract was washed with a 10% solution of alkali (see below for treatment of the alkaline extracts) and with water, dried with magnesium sulfate, and distilled.

2.8 g (72%) of benzene was obtained; b.p. 79.7-78.1 deg, n_D^{20} 1.5005, d_4^{20} 0.8748.

The residue from the benzene distillation was dissolved in alcohol, and the addition of an alcoholic solution of 2, 4-dinitrophenylhydrazine precipitated 0.11 g (1% calculated on the tropylium salt) of the 2, 4-dinitrophenylhydrazone of benzaldehyde, m.p. 237 deg; literature value, m.p. 237 deg; a mixture with a known sample showed no depression of the melting point.

The alkaline extracts were evaporated to a small volume, acidified, and treated with a solution of iodine in potassium iodide and soda. 0.11 g (0.1%) of triiodophenol precipitated, m.p. 157-158 deg; literature value, 157 deg; a mixture with a known sample showed no depression of the melting point.

820 ml of CO (740.4 mm and 20.7 deg, collected over saturated NaCl solution) was evolved during the reaction; this is equivalent to 0.031 mole (62%).

INVESTIGATION OF THE REACTION KINETICS

Aqueous solutions of equimolar amounts of hydrogen peroxide and tropylium bromide were placed in a thermostatted bomb and vigorously agitated (200-240 complete oscillations per minute). The reaction rate was followed by measuring the amount of gas (CO) evolved. It was first shown that the amount of gas formed (during the agitation) was proportional to the amount of material reacted. Rate constants were calculated using the equation:

$$k = \frac{1}{t \cdot C_0}\left(\frac{V_t}{V_\infty - V_t}\right),$$

where t is the time from the beginning of the reaction, V_∞ is the total amount of gas evolved during the reaction (determined experimentally in each experiment), V_t is the amount of gas evolved up to time t, and C_0 is the initial concentration of the reacting substances.

The value of k_t from the beginning of the reaction to 60-70% conversion was used in the determination of k. The values of the apparent activation energy and preexponential factor were determined over the temperature interval 10-50 deg, and were calculated by the method of least squares.

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SIMULTANEOUS DETERMINATION OF C, H, F, AND Cl IN HALOGENATED HYDROCARBONS BY A MICROANALYSIS METHOD

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(Presented by Academician S. S. Medvedev)

A series of investigations have been devoted to the question of the determination of the percentages of C, H, F, and Cl in halogenated hydrocarbons by combustion in a stream of oxygen. N. S. Nikolaev determined three elements (C, H, F) [1], and Teston and McKenna [2] also determined three elements (C, F, Cl). They considered the simultaneous determination of four elements to be impossible in actual practice. M. O. Korshun, N. E. Gel'man and K. I. Glazova [3] showed that it is possible to determine four elements, but the method which they employed for the determination of fluorine was complex; therefore, it was difficult to obtain reproducible results. Proposed methods employing separate determination of the elements have no advantage, since the total time required for the determination of four elements will not be less than that required for the simultaneous determination of C, H, F, and Cl, while the amount of material required for an analysis in the first case will be four times longer than in the last case.

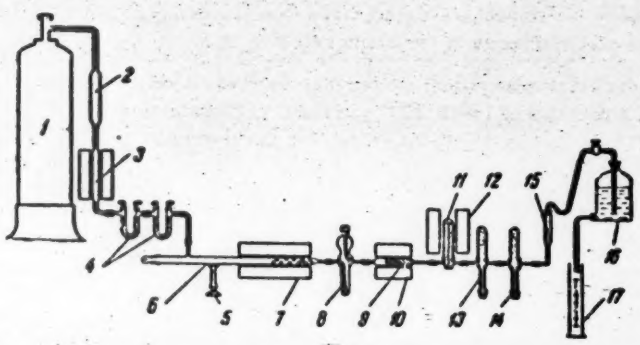

Fig. 1. 1) Oxygen cylinder; 2) drying agent; 3) furnace for combustion of volatile hydrocarbons over platinized asbestos at t° = 485-500°; 4) tubes for absorption of H_2O and CO_2; 5) gas burner for combustion of sample; 6) quartz tube, d = 12 mm, l = 650 mm; 7) furnace at t° = 1050-1150°, d = 15 mm, l = 200-220 mm; 8) vessel containing 98% H_2SO_4 for absorption of H_2O; 9) tube containing metallic Ag for absorption of Cl, d = 10-11 mm, l = 110 mm; 10) furnace at t° = 400° ± 3°, d = 15 mm, l = 110 mm; 11) tube containing KF for absorption of SiF_4, d = 10-11 mm, l = 140 mm; 12) furnace at t° = 240° ± 5°, d = 15 mm, l = 100 mm; 13) tube containing anhydrone $Mg(ClO_4)_2$ for absorption of H_2O; 14) tube containing ascarite for absorption of CO_2; 15) drying agent; 16) water aspirator (dimensions of vessels 13, 14, 15 and 16 were measured by M. O. Korshun [4]); 17) measuring cylinder for determining the rate of flow of oxygen from the volume of water discharged. The oxygen flow rate was usually 10 ml per minute.

The present work established that the simultaneous determination of all of the elements by determination of the weight increase of absorption vessels is actually possible. The proposed method, which was developed on the basis of the work of M. O. Korshun and co-authors [3, 4], permits the determination both of C, F and Cl in halocarbons and of C, H, F and Cl in halogenated hydrocarbons using liquid or solid samples.

The general plan of the apparatus is shown in Figure 1.

Fig. 2. 1) Quartz tube (6); 2) quartz cell; 3) quartz ampoule containing sample.

It was shown experimentally that the length of the absorption vessels (9, 11), the temperature of the furnaces, and the oxygen feed rate are interdependent. The most restricting factors were the length and weight of the absorption vessels, the temperature stability of the furnaces (7, 10, 12), and the chemical purity of the metallic Ag, the KF, H_2SO_4, SiO_2, quartz tube (6), and the quartz ampoules and cell for holding the sample. In order to maintain stable temperatures in furnaces (7, 10 and 12), the furnaces were connected to a voltage regulator. Temperature measurements were made with an accurately calibrated thermocouple when the sample holders were in the furnace.

The KF was prepared by calcining c.p.** KHF_2 for several hours at 450°; the material was then ground, and a fraction with a particle size of d = 1-2 mm was collected. C.p. H_2SO_4 was distilled twice, and average samples taken. The metallic silver was in the form of a screen of fine wire, the purity of which was 99.99%. The joints of vessels (8, 11) were lubricated with a fluorinated grease which was stable to the action of oxygen and fluorine at temperatures above 100°. In order to ensure complete combustion, a small roll of crimped platinum foil 50-60 mm long was placed in quartz tube (6), and the platinum was followed by finely crystalline SiO_2 for more complete conversion of F and HF to SiF_4.

It should be noted that sample combustion had a substantial effect on the analytical results. The most reproducible results were obtained when the sample was first gradually pyrolyzed by means of gas burner (5), and the charred residue then burned by gradual calcination with a soldering torch.

When liquids with boiling points up to ~180° were analyzed, they were placed in quartz ampoules, and, without sealing the end of the ampoule, weighed,* and then placed in the quartz cell as shown in Fig. 2. Higher boiling materials were placed directly in the quartz cell (Fig. 2, 2).

In some cases, the blank combustions showed that there was a weight increase of $5 \cdot 10^{-5}$ g in vessel (8) containing H_2SO_4 and a decrease of $10\text{-}12 \cdot 10^{-5}$ g in vessel (11) containing KF with a corresponding increase in the weight of vessel (13) containing $Mg(ClO_4)_2$; therefore, in determining the percentage compositions, corrections were used in the calculations.

Determination of the percentage contents of the elements consisted of the following operations: 1) 20-30 minutes heating up the apparatus; 2) 30 minutes for blank combustion; 3) 30-45 minutes cooling the vessels; 4) 10-15 minutes weighing; 5) 20-30 minutes heating the vessels; 6) 5-8 minutes purging quartz tube (6) and vessels (8, 9, 11) with oxygen after placing the sample for combustion in the quartz tube. Vessels (13, 14) were then connected into the apparatus; 7) 40-45 minutes for combustion of the samples; 8) 30-40 minutes purging with O_2; 9) 30-40 minutes cooling; 10) 10-15 minutes weighing.

In order to determine the weight increase more accurately, all of the absorption vessels were tared; the weight increase could then be determined by means of the scale and rider only. The gross weight of each absorption vessel did not exceed 12-14 g. The results of analyses of several substances are presented in the table.

As may be seen from Table 1, the proposed method is suitable for all substances boiling above 47°. It should also be noted that this method permits the percentage contents of the elements (H, F, Cl) in various combinations with carbon to be determined without changing the system of the apparatus of Fig. 1. It appears that this method can also be used for the analysis of gaseous substances under conditions such that the rate of flow of

* It was established that with the small capillary openings of the ampoules, there is practically no loss in weight over a period of 10-15 minutes, even for liquids boiling at 50°.

** Chemically pure.

TABLE 1

Determination of the Contents of C, H, F, and Cl in Halogenated Hydrocarbons

Substance analyzed	Sample weight, g	Content, % C Found	C Calc.	H Found	H Calc.	F Found	F Calc.	Cl Found	Cl Calc.	Total % of sample weight	Empirical formula from percentage ratios of the elements
$C_2F_3Cl_3$	0,00711	12,89	12,80	0	0	30,12	30,40	56,54	56,80	99,55	$C_{2,00}F_{3,00}Cl_{1,00}$
	0,00621	13,04				30,24		56,52		99,80	$C_{2,00}F_{3,00}Cl_{1,00}$
$C_2H_2F_2Cl_2$	0,00665	41,83		2,20		24,40		31,27		99,70	$C_{2,00}H_{2,00}F_{2,00}Cl_{2,00}$
	0,00563	41,90	41,92	2,17	2,18	24,79	24,90	30,90	31,00	99,76	$C_{2,00}H_{2,00}F_{2,00}Cl_{2,00}$
$C_2H_2F_2$	0,00553	69,78		5,18		24,58		0	0	99,54	$C_{2,00}H_{2,00}F_{2,00}$
	0,00688	69,77	70,13	5,19	5,20	24,31	24,68			99,27	$C_{2,00}H_{2,00}F_{2,00}$
$C_2H_2F_2Cl$	0,00660	45,25		2,37		35,09		16,82		99,53	$C_{2,00}H_{2,00}F_{2,00}Cl_{1,00}$
	0,00808	45,43	45,18	2,37	2,35	35,27	35,76	16,96	16,71	99,83	$C_{2,00}H_{2,00}F_{2,00}Cl_{1,00}$
$C_2H_2F_2O$	0,00635	50,03		2,10		39,36		0	0	91,49	$C_{2,00}H_{2,00}F_{2,00}O_{1,00}$*
	0,00597	50,02	50,00	2,08	2,08	38,92	39,58	0	0	91,02	$C_{2,00}H_{2,00}F_{2,00}O_{1,00}$
$C_2H_2F_2ClO$	0,00615	42,35		1,30		33,03		15,61		92,29	$C_{2,00}H_{2,00}F_{2,00}Cl_{1,00}O_{1,00}$*
	0,00625	42,33	42,38	1,32	1,32	33,32	33,55	15,68	15,67	92,65	$C_{2,00}H_{2,00}F_{2,00}Cl_{1,00}O_{1,00}$

* Oxygen content by difference

gases equals the rate during the combustion of liquid and solid substances; i.e., a sample weighing $5 \cdot 10^{-3}$ g must be uniformly fed to the combustion over a period of 40-50 minutes.

We consider it to be our duty to express our deep appreciation to Corresponding Member AN SSSR Professor K. A. Kocheshkov and to E. M. Panov for counsel and assistance during the completion of the present work.

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THE EFFECT OF THE ADDITION OF ALKALI ELEMENTS ON THE CATALYTIC PROPERTIES OF CHROMIA-ALUMINA CATALYSTS

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It is well known that the incorporation of small amounts of potassium and cesium into chromia-alumina catalysts increases the yield of valuable products in the aromatization of paraffinic hydrocarbons [1]. However, the literature contains no reliable information on the effect of other alkali elements on the catalytic properties of chromia-alumina catalysts. The present article is devoted to this question. It reports the results of an investigation of the effect of the addition of equivalent amounts of lithium, sodium, potassium, rubidium, and cesium on the activity of two preparations (A and B) of chromia-alumina catalysts with respect to the dehydrocyclization of n-heptane and the dehydrogenation of cyclohexane at 520°.

It was found that the addition of lithium to our chromia-alumina catalysts had practically no effect on the yield of aromatics from heptane. The introduction of sodium into catalysts A and B increased the yield of aromatics by 8%. The promoting effect of the alkali elements increased further with potassium (increase in the yield of aromatics by 13 and 11%), reached a maximum with rubidium (21 and 15%), while cesium increased the yield by 9 and 13%. The promoting effect of the alkali elements was also observed in the dehydrogenation of cyclohexane over these same samples of catalyst. Since the catalysts tested did not decrease in activity over a period of 4 hours both with heptane and with cyclohexane feed (see also our previous article [2]), it follows that the yields of aromatics over the different samples reflect the change in their activity due to the addition of promoters, and that the changes were not due to changes in stability with time during the course of the experiments.

It should be pointed out that there is a great similarity between the effect of the different alkali elements on the dehydrocyclization of heptane over chromia-alumina catalysts and the effect of these same promoters on the dehydrogenation of butene over iron-magnesia catalyst [3]. It is possible that this similarity is explained by the presence of a stage common to dehydrocyclization and dehydrogenation reactions of hydrocarbons. This stage could be dissociative adsorption on the catalyst of paraffin molecules or the saturated part of olefin molecules, i.e., activated adsorption with simultaneous deformation or dissociation of the carbon–hydrogen bonds of those atoms of the molecule of hydrocarbon which participate in the reaction.

The introduction of alkali elements into chromia-alumina catalyst increases the yield of catalyzate, i.e., cracking of the hydrocarbons is decreased. This compels us to assume that in a chromia-alumina catalyst there are active centers catalyzing cracking reactions and the polymerization of unsaturated hydrocarbons, which proceed through the formation of carbonium ions as in the classical case of silica-alumina catalyst. The action of the addition of alkali elements is apparently to decrease the deposition of "coke" on the catalyst and, consequently, to increase the stability of catalyst [4]. Since the alkali elements are catalysts for the oxidation of carbon [5] and "coke" by steam [3], it would be expected that the introduction of alkali elements would decrease the regeneration temperature of the catalysts thereby increasing their stability, i.e., lengthening their life. On the other hand, the presence of alkali elements decreases the thermal stability of chromia-alumina catalysts [4]. Thus, the alkali elements apparently have a combination effect on the catalyst during aromatization of hydrocarbons, the different aspects of which are still not sufficiently clear.

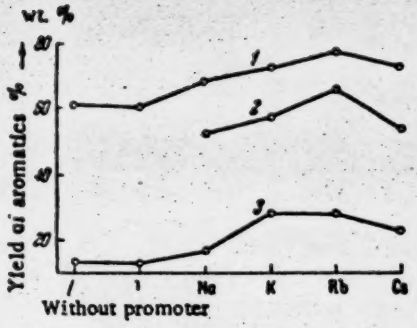

Fig. 1. Yields of aromatics from heptane over chromia-alumina catalysts promoted with alkali elements. Space rate, 0.35 hours^{-1}; run time, 4 hours. 1) Catalyst B, run temperature 530°; 2) catalyst A, run temperature 520°; 3) yield of butadiene from butenes over iron-magnesia catalyst [3].

EXPERIMENTAL

The experimental method and the apparatus used in the present investigation were the same as in our previous work [2]. The hydrocarbons had the following constants:

	B.p., °C 760 mm	n_D^{20}	d_4^{20}	M.p., °C
Cyclohexane	80.7	1.4260	——	+ 6.3
n-Heptane	98.4	1.3878	0.6834	——

Catalysts A and B, on which the promoters were deposited, had the same composition (15 mole % chromium oxide and 85 mole % aluminum oxide), but they differed somewhat in their method of preparation. Each of the preparations of catalysts A and B was divided into portions of equal weight, which were then impregnated under uniform conditions with a solution of the desired element, the solutions being used in amounts such that the promoted catalysts had the following composition: 2.6 mole % alkali element oxide, 14.6 mole % chromium oxide, and 82.8 mole % aluminum oxide. The catalyst samples were dried, heated to the temperature of the experiment in a stream of air, and activated by passing hydrocarbon over the catalyst at the temperature of the experiment for a period of 2 or 4 hours with subsequent regeneration. The contents of aromatic and unsaturated hydrocarbons in the liquid reaction products were determined by methods described previously [2].

Aromatization of heptane. We carried out two series of experiments on the aromatization of n-heptane, one with catalyst A and the other with catalyst B. The first series of experiments, with catalyst A, was carried out in parallel with the experiments on the dehydrogenation of cyclohexane in a furnace block designed to take two catalyst tubes simultaneously. This method of carrying out the experiment provided assurance that the observed difference in the effects of the various members of the alkali element group on both reactions was not due to a difference in temperature. These experiments, which were of 4 hours duration with catalysts A, were carried out at 520° at a space rate of 0.35 hours^{-1}; 20 ml of catalyst A was used in each run. The results of the experiments are presented in Table 1 and in Figure 1. The introduction of sodium into catalyst A increased the yield of aromatics from 44 wt. % (unpromoted catalyst) to 52%, the introduction of potassium — to 57%, of rubidium — to 65%, and of cesium — to 53%.

The second series of experiments was carried out at 530° and a space rate of 0.35 hours^{-1} using catalyst samples prepared from catalyst B (20 ml), after which, experiments with cyclohexane were carried out over these catalyst samples. The yield of aromatics with catalyst B (see Table 1 and Figure 1) was 61 wt. %.

With the introduction of lithium, the yield of aromatics was unchanged (60%); the addition of sodium increased the yield to 69%, potassium — to 72%, rubidium — on the average of 76%, cesium — to 74%.

Figure 1 also shows the relation between the yield of butadiene from butene and the alkali element used as the promoter for a copper-containing iron-magnesia catalyst [3]. The great similarity of this relation in the dehydrocyclization of heptane to that in the dehydrogenation of benzene is evident from a comparison of the course of the curves in Figure 1.

Aromatization of cyclohexane. Two series of experiments were also carried out with cyclohexane. The first series was carried out at 520° and a space rate of 0.8 hours^{-1} using catalysts prepared by the deposition of the salts on catalyst A (10 ml for each catalyst). Two experiments, one directly after the other without regeneration, were carried out with the unpromoted catalyst and with the potassium- and sodium-containing catalysts. The yields of aromatics in these experiments (see Table 2 and Figure 2) were practically the same, which indicates the absence of catalyst poisoning. The yield of aromatics was 30 wt. % with unpromoted catalyst A, while with the promoted catalysts, it averaged 35%; the experimental scatter of the results did not exceed ± 2%. We

TABLE 1

Aromatization of Heptane Over Chromia-Alumina Catalysts. Experiment Temperatures: 520° with Catalyst A, 530° with Catalyst B; Space Rate 0.35 hours^{-1}.

Expt. No.	Catalyst	Promoter	n_D^{20}	Bromine No. of catalyzate	Yield, wt. %		
					catalyzate	aromatics	unsaturates
1	A	Without promoter	1,4540	14,7	65	44	9,0
2		Na	1,4562	13,6	75	52	8,3
3		K	1,4580	13,8	80	57	8,5
4		Rb	1,4856	—	70	65	—
5		Cs	1,4545	10,4	77	53	6,4
6	B	Without promoter	1,4660	15,76	84	59	9,7
7		Same	1,4610	15,34	84	62	9,4
8		Same	1,4590	15,76	85	61	9,7
9		Li	1,4589	16,40	83	60	10,1
10		Na	1,4665	2,00	89	70	1,2
11		Na	1,4667	1,20	89	69	0,7
12		K	1,4728	7,85	87	72	4,8
13		Rb	1,4780	5,90	89	78	3,6
14		Rb	1,4760	5,44	87	74	9,9
15		Cs	1,4720	6,05	90	74	3,8
16		Cs	1,4720	5,75	90	74	3,1

TABLE 2

Aromatization of Cyclohexane; Temperature, 520°; run time, 4 Hours.

Expt. No.	Promoter	n_D^{20} of catalyzate	Bromine No. of catalyzate	Yield, wt. %		
				catalyzate	aromatics	unsaturates
Over chromia-alumina catalyst A[1]						
1	Without promoter	1,4472	4,5	85	30	2,3
2[2]	Same	1,4450	5,1	84	28	2,6
3	Li	1,4500	—	92	36	—
4	Na	1,4500	4,0	85	33	2,0
5[3]	Na	1,4542	3,0	87	39	1,5
6	K	1,4511	3,7	89	36	1,9
7[2]	K	1,4528	2,9	86	37	1,5
8	K	1,4519	2,1	85	36	1,1
9[3]	K	1,4540	2,3	88	39	1,2
10	Rb	1,4580	—	71	35	—
11	Rb	1,4510	1,6	87	35	0,8
12	Cs	1,4488	2,7	90	33	1,4
Over chromia-alumina catalyst B[4]						
1	Without promoter	1,4812	4,12	88	69	2,1
2[2]	Same	1,4800	5,63	91	71	2,9
3	Li	1,4823	2,99	93	73	1,5
4	Li	1,4807	3,20	97	75	1,6
5	Na	1,4868	1,87	93	80	0,96
6	K	1,4869	1,20	92	79	0,6
7	Rb	1,4835	2,75	89	73	1,2
8	Rb	1,4855	2,30	89	74	1,1
9	Cs	1,4812	2,70	91	71	1,3
10	Cs	1,4845	2,45	91	75	1,2

[1] Space rate, 0.8 hours^{-1}. [2] Experiment carried out after the preceding experiment without regeneration. [3] Experiment carried out for 3 hours after the preceding experiment without regeneration. [4] Space rate, 0.35 hours^{-1}. [5] Fresh portion of catalyst.

decided to obtain a higher yield of aromatics when carrying out the second series of experiments, with catalyst B. With this aim, the experiments were carried out at a space rate of 0.35 hours^{-1} (20 ml of catalyst) and a temperature of 520°. The yield of aromatics with unpromoted catalyst B was 70 wt. %, and it averaged 75% with the promoted catalysts (see Table 2 and Figure 2). The variance among the data of this series of experiments was ± 3.5%. Thus, the increase in the yield of aromatics attributable to the use of promoted catalysts in place of unpromoted catalyst was 5% for both catalyst A and B.

It should be pointed out that the yields of unsaturated hydrocarbons in experiments with samples of promoted catalysts were lower than in experiments with unpromoted samples (see Tables 1 and 2), both with heptane and with cyclohexane. However, the alkali elements, with the exception of lithium, are promoters for

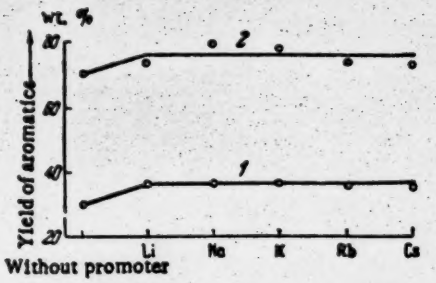

Fig. 2. Yields of aromatics from cyclohexane over chromia-alumina catalysts promoted with alkali elements. Experiment temperature, 520°; test duration, 4 hours; 1) average yields of aromatics with catalysts prepared from catalyst A, space rate 0.8 hours^{-1}; 2) average yields of aromatics with catalysts prepared from catalyst B, space rate 0.35 hours^{-1}.

the dehydrogenation of those hydrocarbons which, by virtue of their structure, are incapable of dehydrocyclization [1, 3, 4]. This difference can apparently be explained on the basis that the unsaturated hydrocarbons formed from heptane and cyclohexane are converted to aromatics at a still greater rate. It is possible that there is also apparent here the effect of the hydrogen and aromatics formed on the thermodynamic equilibria of the systems heptane - - heptene [6] and cyclohexane - cyclohexene. The assumption follows that in chromia-alumina-catalyzed dehydrogenation reactions of paraffins containing not more than five carbon atoms in the longest chain, the alkali elements promote the dehydrogenation reaction.

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POLYMERIZATION OF VINYLAROMATIC ORGANOSILICON COMPOUNDS

DERIVATIVES OF α-METHYLSTYRENE

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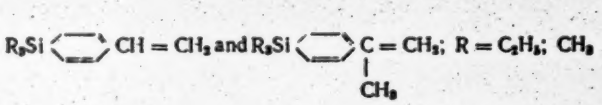
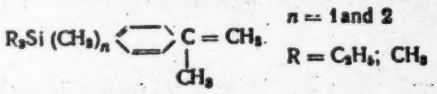
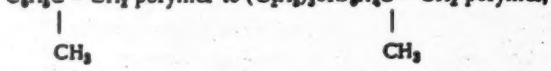
We have previously investigated the polymerization activity of vinylaromatic organosilicon compounds containing a silicon attached to a carbon of the benzene ring [1]:



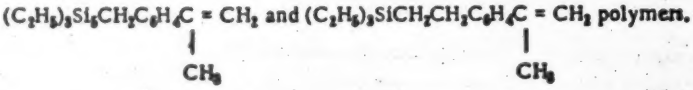
Glassy polymers were obtained, and their properties were determined. The present communication describes the polymerization of vinylaromatic compounds which are derivatives of α-methylstyrene containing a silicon attached to the benzene ring through methylene groups:



The polymerization was carried out under a pressure of 6000 atm, in the presence of radical-type initiators, azobisisobutyronitrile (ABN) and tertiary butyl peroxide (TBP). A comparison of the results of the polymerizations carried out with ABN and TBP shows that the polymerization proceeds at a higher rate in the presence of an 0.3 mole % concentration of azobisisobutyronitrile at a temperature of 80° than in the presence of a 1 mole % concentration of tertiary butyl peroxide at 130°. Correspondingly, polymers with a higher molecular weight were obtained in the first case (see Table 1). A comparison of the intrinsic viscosities of polymers of α-methylstyrene and of silicon derivatives of α-methylstyrene shows that the viscosity decreases from



then further decreases to:



The thermomechanical properties change in the same order (see Figure 2).

TABLE 1

Polymerization of α-Methylstyrene and its Derivatives Under a Pressure of 6000 Atm. for 6 Hours

Expt. No.	Monomer	Polymerization conditions: Initiator	Polymerization conditions: Init. conc., mole %	Polymerization conditions: temp. °C	Polymer yield, % of monomer	$[\eta]_{100}$ ml/g
1	$C_6H_5C(CH_3) = CH_2$	ABN	0,3	80	82,0	1,43
2	$C_6H_5C(CH_3) = CH_2$	TBP	1,0	130	68,0	0,52
3	$(C_2H_5)_3SiC_6H_4C(CH_3) = CH_2$	ABN	0,3	80	64,0	0,92
4*	$(C_6H_5)_3SiC_6H_4C(CH_3) = CH_2$	TBP	1,0	120	49,4	0,46
5	$(C_2H_5)_3SiCH_2C_6H_4C(CH_3) = CH_2$	ABN	0,3	80	42,9	0,76
6	$(C_2H_5)_3SiCH_2C_6H_4C(CH_3) = CH_2$	TBP	1,0	130	14,6	0,30
7	$(C_2H_5)_3SiCH_2CH_2C_6H_4C(CH_3) = CH_2$	ABN	0,3	80	31,9	0,72
8	$(C_2H_5)_3SiCH_2CH_2C_6H_4C(CH_3) = CH_2$	TBP	1,0	130	17,6	0,26
9	$(CH_3)_3SiCH_2C_6H_4C(CH_3) = CH_2$	TBP	1,0	130	20,0	0,41

* Experiment carried out previously [1].

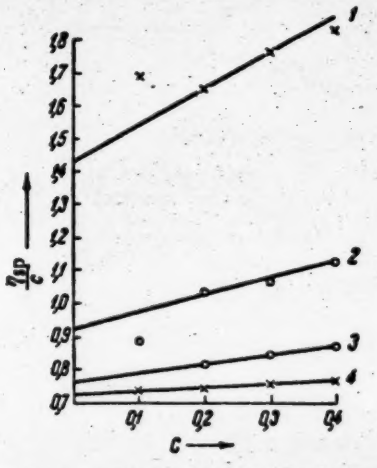


Fig. 1. Intrinsic viscosity of polymers prepared in the presence of ABN: 1) $C_6H_5C(CH_3) = CH_2$ polymer; 2) $(C_2H_5)_3SiC_6H_4C(CH_3) = CH_2$ polymer; 3) $(C_2H_5)_3SiCH_2C_6H_4C(CH_3) = CH_2$ polymer; 4) $(C_2H_5)_3SiCH_2CH_2C_6H_4C(CH_3) = CH_2$

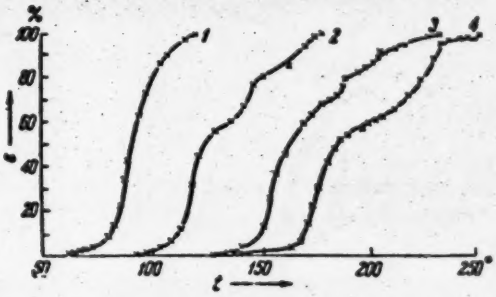


Fig. 2. Variation in deformation with temperature for samples of polymers prepared in the presence of ABN: 1) $(C_2H_5)_3SiCH_2CH_2C_6H_4C(CH_3) = CH_2$ polymer; 2) $(C_2H_5)_3Si_5CH_2C_6H_4C(CH_3) = CH_2$ polymer; 3) $(C_2H_5)_3SiC_6H_4C(CH_3) = CH_2$ polymer; 4) $C_6H_5C(CH_3) = CH_2$

EXPERIMENTAL

The monomers were synthesized by methods previously developed by us [2]. Investigation of the polymerization was carried out under previously described standard conditions [1]. About 2 ml of monomer was charged to each ampoule. The polymerization products were purified by reprecipitation from benzene with methyl alcohol, and were dried to constant weight at 50° under vacuum. After reprecipitation, the polymers prepared in the presence of azobisisobutyronitrile were colorless fibrous products, while the polymers prepared with tertiary butyl peroxide were powders. All of the polymers corresponded in elemental composition to the formulas of their respective monomers.

The results of the experiments under pressure are presented in Table 1. Formation of polymer was not detected in experiments in which elevated pressure was not used. The relative viscosity of the polymers was measured with an Ostwald viscosimeter at 20° in toluene. The intrinsic viscosity was determined graphically from these data (Figure 1). The thermomechanical curves were determined by the method of reference [1] and are presented in Figure 2.

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[2] A. D. Petrov, E. A. Chernyshev and N. G. Tolstikova, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1959).*

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* Original Russian pagination. See C.B. Translation.

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A STUDY OF THE ADDITION OF TRIALKOXYSILANES TO OLEFINS

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Up to the present time, there has been no information on the possibility of adding trialkoxysilanes to olefins. In 1948, Pietrusza, Sommer and Whitmore [1] reported that triethoxysilane does not add to 1-octene under the influence of acetyl peroxide and ultraviolet radiation as reaction initiators. The single indication of the possibility of adding triethoxysilane to olefins is to be found in a patent issued to Wagner [2].

TABLE 1

Compound	B.p.		n_D^{20}	d_4^{20}
	°C	mm Hg		
HSi $(OC_2H_5)_3$	135	755	1,3788	
HSi (iso-$OC_3H_7)_3$	104	4	1,4025	0,8565
HSi $(OC_4H_9)_3$	105	2	1,4100	0,8881
HSi (sec -$OC_4H_9)_3$	70	2	1,4030	0,8668
HSi (iso-$OC_4H_9)_3$	103	3	1,4025	0,8661
HSi (tert -$OC_4H_9)_3$	186	755	1,3969	0,8547

We have shown that it is possible to add trialkoxysilanes to olefins by reacting triethoxysilane, triisopropoxysilane, tributoxysilane, tri(sec-butoxy) silane, and tri(tert-butoxy) silane with 1-nonene and 1-decene in the presence of chloroplatinic acid and of platinized carbon. The physicochemical properties of the initial trialkoxysilanes are presented in Table 1.

TABLE 2

Compound	n_D^{20}	d_4^{20}	MR_D		B.p.		Yield, %
			found	calc.	°C	mm Hg	
$C_9H_{17}Si$ (tert -$OC_4H_9)_3$	1,4200	0,8650	105,50	106,64	138—140	2	18,2
$C_9H_{17}Si$ $(OC_4H_9)_3$	1,4280	0,8747	106,10	106,64	155—158	2	21,1
$C_9H_{19}Si$ $(OC_2H_5)_3$	1,4182	0,8827	82,87	83,49	130—133	2	41,4
$C_9H_{19}Si$ (iso -$OC_3H_7)_3$	1,4180	0,8589	97,57	97,38	128—132	2	64,9
$C_9H_{19}Si$ $(OC_4H_9)_3$	1,4298	0,8715	111,01	111,27	164—166	2	43,1
$C_9H_{19}Si$ (sec -$OC_4H_9)_3$	1,4270	0,8714	111,00	111,27	160—164	2	37,8
$C_9H_{19}Si$ (tert -$OC_4H_9)_3$	1,4232	0,8622	110,70	111,27	150—155	2	12,5
$C_9H_{19}Si$ (iso -$OC_4H_9)_3$	1,4260	0,8700	110,40	111,27	175—176	4	78,4
$C_{10}H_{21}Si$ $(OC_4H_9)_3$	1,4315	0,8710	115,30	115,90	167—170	2	65,2
$C_{10}H_{21}Si$ (tert -$OC_4H_9)_3$	1,4260	0,8589	115,90	115,90	160—161	2	20,5

TABLE 3

Product prepared by addition reaction				Formula	Product prepared by interaction of alkyltrichlorosilane with alcohol			
		B.p.			B.p.			
d_4^{20}	n_D^{20}	°C	mm Hg		°C	mm Hg	n_D^{20}	d_4^{20}
0,8589	1,4180	128—132	2	$C_9H_{19}Si(iso\text{-}OC_3H_7)$	131—133	2	1,4182	0,8591
0,8710	1,4315	167—171	2	$C_{10}H_{21}Si(OC_4H_9)_3$	172—173	2	1,4320	0,8711

In the presence of chloroplatinic acid, the addition of trialkoxysilanes to olefins proceeds with yields of 30-40%. However, the addition of tri(ter-butoxy) silane to olefins proceeds with low yields (12%) owing to steric hindrance. The physicochemical properties of the alkyltrialkoxysilanes prepared are presented in Table 2.

Decyltributoxysilane and nonyltriisopropoxysilane were also prepared by an alternate synthesis – by the interaction of nonyltrichlorosilane and decyltrichlorosilane with the appropriate olefins:

$$C_{10}H_{21}SiCl_3 + 3C_4H_9OH \rightarrow C_{10}H_{21}Si(OC_4H_9)_3,$$

$$C_9H_{19}SiCl_3 + 3iso\text{-}C_3H_7OH \rightarrow C_9H_{19}Si(iso\text{-}OC_3H_7)_3.$$

As may be seen from the data of Table 3, the physicochemical properties of the alkyltrialkoxysilanes prepared by the addition of trialkoxysilanes to olefins were identical to those of the alkyltrialkoxysilanes prepared by the interaction of alkyltrichlorosilanes with alcohols. The Raman spectra of the nonyltriisopropoxysilanes prepared by the two methods were also identical with respect to the number and intensity of the lines.

The comparison of the physicochemical properties and spectra of the alkyltrialkoxysilanes prepared by addition and by the alternate synthesis provides a basis for the assumption that the addition proceeds contrary to Markovnikov's rule:

$$HSi(OAlk)_3 + RCH = CH_2 \rightarrow RCH_2 - CH_2 - Si(OAlk)_3.$$

EXPERIMENTAL

a) Addition of trialkoxysilanes to olefins in the presence of chloroplatinic acid. The addition of the trialkoxysilanes to olefins was carried out in a three-necked flask fitted with a stirrer, a reflux condenser, a thermometer, and a dropping funnel. The olefin and a 10% solution of chloroplatinic acid in absolute isopropyl alcohol were charged to the flask. The mixture was heated to 60°, and the trialkoxysilane was then added dropwise from the dropping funnel at a rate such that the temperature in the flask did not exceed 100-110°. The reaction mixture was then heated for 2-3 hours at 100° and fractionated.

The trialkoxysilanes were prepared by the interaction of trichlorosilane and the appropriate alcohols in solution in toluene in the presence of pyridine. 1-Octene, 1-nonene, and 1-decene were prepared by pyrolysis of the corresponding acetates at 450-500°; their properties were in agreement with the literature values.

Nonyltriethoxysilane. From 24.6 g (0.15 mole) of triethoxysilane, 18.9 g (0.15 mole) of 1-nonene, and 1 ml of the chloroplatinic acid solution was obtained 18 g (41.4% yield) of nonyltriethoxysilane; b.p. 130-133° at 2 mm.

Found %: C 62.31; 62.16; H 11.90; 11.85 $C_{15}H_{34}SiO_3$. Calculated %: C 62.30; H 11.80

Nonyltriisopropoxysilane. From 30.9 g (0.15 mole) of triisopropoxysilane, 18.9 g (0.15 mole) of 1-nonene, and 1 ml of the chloroplatinic acid solution was obtained 32.3 g (64.9% yield) of nonyltriisopropoxysilane; b.p. 128-132° at 2 mm.

Found %: C 65.23; 65.16; H 12.23; 12.16 $C_{18}H_{40}SiO_3$. Calculated %: C 65.02; H 12.11

The following frequencies were present in the Raman spectrum: 432(1), 454(1), 624(0), 635(1), 663(3), 871(4-5), 888(3), 894(3), 935(2), 1009(0), 1018(0), 1029(1), 1039(1), 1080(1), 1131(1), 1176(2), 1205(1), 1214(0), 1226(0), 1308(3), 1333(2), 1356(3), 1387(0), 1412(0), 1450(110).

Nonyltributoxysilane. From 37.2 g (0.15 mole) of tributoxysilane, 18.9 g (0.15 mole) of 1-nonene, and 1 ml of the chloroplatinic acid solution was obtained 24.2 g (43.1% yield) of nonyltributoxysilane; b.p. 164-166° at 2 mm.

Found %: C 67.42; 67.31; H 12.42; 12.44 $C_{21}H_{46}SiO_3$. Calculated %: C 67.33; H 12.51

Nonyltri(sec-butoxy)silane. From 37.2 g (0.15 mole) of tri(sec-butoxy)silane, 18.9 g (0.15 mole) of 1-nonene, and 1 ml of the chloroplatinic acid solution was obtained 21.2 g (37.8% yield) of nonyltri(sec-butoxy)silane; b.p. 160-164° at 2 mm.

Found %: C 67.01; 66.92 H 12.23; 12.31 $C_{21}H_{46}SiO_3$. Calculated %: C 67.33; H 12.51

Nonyltri(isobutoxy)silane. From 37.2 g (0.15 mole) of triisobutoxysilane, 18.9 g (0.15 mole(of 1-nonene, and 1 ml of the chloroplatinic acid solution was obtained 44 g (78.4% yield) of nonyltriisobutoxysilane; b.p. 175-176° at 4 mm.

Found %: C 67.51; 67.41; H 12.36; 12.39 $C_{21}H_{46}SiO_3$. Calculated %: C 67.33; H 12.51

Nonyltri(ter-butoxy)silane. From 37.2 g (0.15 mole) of tri(ter-butoxy)silane, 18.9 g (0.15 mole) of 1-nonene, and 1 ml of the chloroplatinic acid solution was obtained 7 g (12.5% yield) of nonyltri(tert-butoxy)silane; b.p. 150-155° at 2 mm.

Found %: C 67.33; 67.39; H 12.30; 12.38 $C_{21}H_{46}SiO_3$ Calculated %: 67.33; H 12.51

Decyltributoxysilane. From 25 g (0.1 mole) of tributoxysilane, 15 g (0.1 mole) of 1-decene, and 1 ml of the chloroplatinic acid solution was obtained 23 g (61.5% yield) of decyltributoxysilane; b.p. 167-171° at 2 mm.

Found %: C 68.07; 67.94; H 12.39; 12.43 $C_{22}H_{48}SiO_3$. Calculated %: C 68.01; H 12.45

Decyltri(tert-butoxy)silane. From 25 g (0.1 mole) of tri(tert-butoxy)silane, 28 g (0.2 mole) 1-decene, and 1 ml of the chloroplatinic acid solution was obtained 24 g (65% yield) of decyltri(ter-butoxy)silane; b.p. 160-162° at 2 mm.

Found %: C 68.00; 68.02; H 12.54; 12.40 $C_{22}H_{48}SiO_3$. Calculated %: C 68.01; H 12.45

b) Addition of trialkoxysilanes to olefins in the presence of platinized carbon. The addition of tributoxysilanes to olefins in the presence of platinized carbon was carried out in sealed glass tubes which were placed in a Carius-type furnace and heated at 200° for 20 hours.

Octyltributoxysilane. From 25 g (0.1 mole) of tributoxysilane and 22 g (0.2 mole) of 1-octene in the presence of 0.1 g of platinized carbon was obtained 7.6 g (21.1% yield) of octyltributoxysilane. B.p. 160-163° at 2 mm.

Found %: C 66.47; 67.32; H 12;40; 12.46 $C_{20}H_{44}SiO_3$. Calculated %: C 66.60; H 12.30

Octyltri(tert-butoxy)silane. From 12.5 g of tri(tert-butoxy)silane and 11.2 g (0.1 mole) of 1-octene in the presence of 0.1 g of platinized carbon was obtained 3.3 g (18.2% yield) of octyltri(ter-butoxy)silane; b.p. 138-140° at 2 mm.

Found %: C 65.92; 65.95; H 12.36; 12.30 $C_{20}H_{44}SiO_3$. Calculated %: C 65.60; H 12.30

Decyltributoxysilane. From 25 g (0.1 mole) of tributoxysilane and 28 g (0.2 mole) of 1-decene in the presence of 0.1 g of platinized carbon was obtained 25 g (65.2% yield) of decyltributoxysilane; b.p. 167-170° at 2 mm.

Found %: C67.87; 67.85; H 12.45; 12.51 $C_{22}H_{48}SiO_3$. Calculated %: C 68.01; H 12.45

Decyltri(tert-butoxy)silane. From 25 g (0.1 mole) of tributoxysilane and 28 g (0.2 mole) of 1-decene in the presence of 0.1 g of platinized carbon was obtained 7 g (18% yield) of decyltri(tert-butoxy)silane;b.p. 160-164° at 2 mm.

Found %: C 68.09; 67.94; H 12.43; 12.54 $C_{22}H_{48}SiO_3$. Calculated %: C 68.01; H 12.45

c) Preparation of alkyltrialkoxysilanes by the interaction of alkyltrichlorosilanes with alcohols.

Nonyltriisopropoxysilane. 47 g (0.17 mole) of nonyltrichlorosilane was added, with stirring, to a mixture of 150 ml of toluene, 56 g of pyridine, and 92 g (0.51 mole) of absolute isopropyl alcohol. The precipitate was filtered. Fractionation of the liquid product gave 33.5 g (56.2% yield) of nonyltriisopropoxysilane. B.p. 131-133° at 2 mm.

Found %: C 65.20; 65.11; H 12.09; 12.34 $C_{18}H_{38}SiO_3$. Calculated %: C 65.02; H 12.11

The following frequencies were present in the Raman spectrum: (cm^{-1}): 432(1); 454(1); 624(0); 635(1); 663(3); 871(4-5), 883(3), 894(3), 935(2); 1009(0), 1018(0), 1029(1), 1039(1), 1131(1), 1176(2), 1205(1), 1241(0), 1226(0), 1308(3), 1333(2), 1356(3), 1387(0), 1412(0), 1450 and (10).

Decyltributoxysilane. 42 g (0.15 mole) of decyltrichlorosilane* was added, with stirring, to 100 ml of toluene, 48 g of pyridine, and 102 g (0.45 mole) of absolute butyl alcohol. The precipitate was filtered. Fractionation gave 39 g (66.2% yield) of decyltributoxysilane. B.p. 172-173° at 2 mm.

Found %: C 67.94; 67.99; H 12.31; 12.28 $C_{22}H_{48}SiO_3$. Calculated %: C 68.01; H 12.45

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[2] G. Wagner, U. S. Pat. 2,637,737; Chem. Abstr. 8254 (1954).

[3] A. V. Topchiev, N. S. Nametkin and T. I. Chernysheva, Proc. Acad. Sci. USSR, 115, 326 (1957).

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* The nonyltrichlorosilane and decyltrichlorosilane were prepared by the additionof trichlorosilane to 1-nonene and 1-decene, respectively, in the presence of benzoyl peroxide [3].

VISCOSITY-TEMPERATURE PROPERTIES OF HIGH-MOLECULAR-WEIGHT HYDROCARBONS OF MIXED STRUCTURE

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(Presented by Academician A. A. Balandin, January 13, 1959)

The viscosity of hydrocarbons is one of the major properties directly connected with chemical structure. The change in viscosity with temperature is one of the most important performance characteristics of lubricating oils. As investigations carried out in recent years have shown the hydrocarbons present in the lubricating-oil fraction of petroleum have a mixed (hybrid) structure. Therefore, it is very essential to trace the dependence of viscosity on the molecular structure of hydrocarbons of this mixed type and, in particular, to follow the nature of the changes in the viscosity–temperature relation. The effect of benzene, cyclohexyl, and cyclopentyl rings introduced into the paraffin chain on the viscosity–temperature relationship of hydrocarbons has been studied by Schiessler and co-workers [2, 3]. Hydrocarbons of the most complex mixed structure containing in the molecule, in addition to paraffin, cycloparaffin, and benzene structural units, condensed rings of the type of naphthalene, tetralin, and decalin have not been studied up to the present time. Furthermore, the high-molecular-weight fraction of petroleum contains a considerable amount of such structural types.

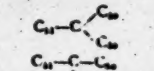
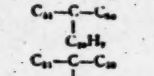
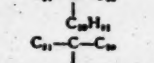
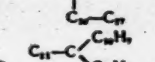
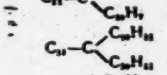
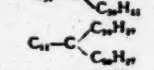
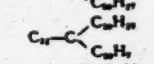
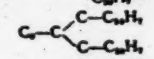
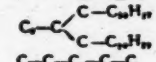
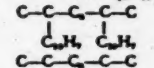
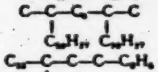
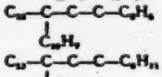
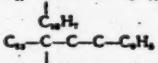
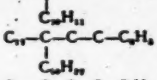
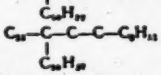
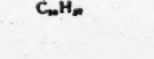
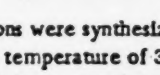
TABLE 1

Properties and Structures of Newly Synthesized Hydrocarbons

Expt. No.	Hydrocarbon	B.p., °C at 0.3 mm	n_D^{20}	d_4^{20}	Method of preparation
1	11-(α-Naphthyl)docosane	216	1,5200	0.9005	Lauronaphthone + decyl-Mg Br
2	11-(α-Tetrahydronaphthyl)docosane 1	218	1.4946	0.8857	Hydrogenation of hydrocarbon No. 1
3	11-(α-Decahydronaphthyl)docosane	220	1.4775	0.8668	Hydrogenation of hydrocarbon No. 1
4	1-Phenyl-3-(α-naphthyl)hexadecane	220	1.5550	0.9568	From myristonaphthone and phenethylmagnesium bromide
5	1-Phenyl-3-(α-tetrahydronaphthyl)-hexadecane	220	1.5250	0.9380	Hydrogenation of hydrocarbon No. 4
6	1-Phenyl-3-(β-decahydronaphthyl)-hexadecane	218	1.5090	0.9158	From myristodecahydronaphthone and phenethylmagnesium bromide
7	1-Cyclohexyl-3-(α-naphthyl) hexadecane	223	1.5348	0.9313	From myristonaphthone and 2-cyclohexyl-1-ethylmagnesium bromide
8	1-Cyclohexyl-3-(α-decahydronaphthyl)hexadecane	225	1.5040	0.9105	Hydrogenation of hydrocarbon No. 4

The aim of the present work was to fill in this gap. First of all, it was necessary to determine the effect of the number of naphthalene, decalin, and tetralin rings and their position in the molecule on the viscosity properties of the hydrocarbon. For this purpose, hydrocarbons of the naphthalene, tetralin, and decalin series containing 32 carbon atoms in the molecule were synthesized. The properties of the newly synthesized hydrocarbons are presented in Table 1; the previously synthesized hydrocarbons have already been described [1].

TABLE 2

Expt. No.	Hydrocarbon	Kinematic viscosity at different temperatures (in centistokes)							
		20°	40°	60°	80°	100°	120°	140°	160°
1		31,62	15,97	8,86	5,68	3,97	2,95	2,29	1,98
2		104,5	37,40	16,02	8,92	5,58	3,92	2,80	2,27
3		111,0	38,65	16,45	9,06	5,64	3,97	2,82	2,19
4		116,0	40,37	18,71	10,31	6,33	4,36	3,13	2,39
5		17910	1536	254,2	69,7	26,4	12,52	7,07	4,57
6		3981	478,7	111,3	38,4	17,04	9,50	5,81	3,98
7		7328	653,1	135,3	44,3	19,0	10,42	6,29	4,46
8		3200	398	98,5	34,2	16,43	9,39	5,91	4,40
9		5420	485	97,50	31,70	13,55	7,37	4,65	3,32
10		4265	450	97,20	34,50	16,07	9,12	5,73	4,04
11		2838	398	93,10	33,05	15,10	8,48	5,44	3,82
12		2786	335,0	83,60	33,00	16,12	9,55	6,22	4,41
13		180,7	50,3	21,50	10,82	6,64	4,44	3,19	2,44
14		338,8	92,8	34,8	16,60	9,26	5,86	4,04	3,02
15		227,0	63,1	24,2	12,13	7,13	4,70	3,35	2,55
16		184,7	54,10	22,85	11,70	7,10	4,78	3,41	2,61
17		549,5	123,0	41,70	19,30	10,45	6,56	4,43	3,26

The hydrocarbons were synthesized by Grignard synthesis. The tertiary alcohols were dehydrated over pure aluminum oxide at a temperature of 320° and a pressure of 1 mm Hg. Hydrogenation was carried out in the presence of Raney nickel in an autoclave at a hydrogen pressure of 150 atm, and at a temperature of 70° for the double bond and a temperature of 150° for hydrogenation of the naphthalene ring to decalin. Hydrogenation of the naphthalene ring to a tetralin ring was carried out in the presence of copper–chromium catalyst at a temperature of 200° and a pressure of 250 atm. The resulting hydrocarbons were distilled in a special packed column having an efficiency of 8 theoretical plates; following the distillation, which was carried out at a pressure of 0,3 mm, the hydrocarbons were additionally purified with aluminum oxide or silica gel. The viscosity of all hydrocarbons was measured at eight temperatures, using an Ostwald – Pinkevich viscosimeter with a capillary diameter of 2,0 – – 0,8 mm. The results of the measurements are presented in Table 2.

Replacement of ten carbon atoms of the paraffin chain by a naphthalene, tetralin, or decalin ring led to an increase in the viscosity by a factor of 2-3; further replacement of successive units of ten carbon atoms of the paraffin chain by, respectively, a naphthalene, tetralin, or decalin ring led to a sharp increase in the viscosity by a factor of approximately 8-17.

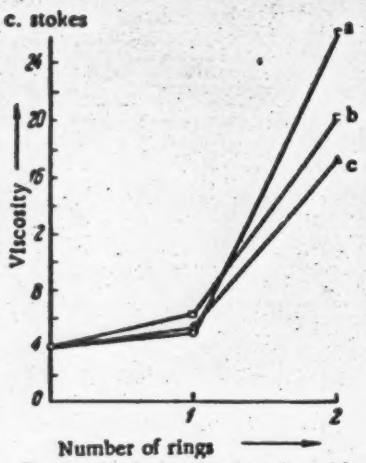


Fig. 1. Variation in viscosity with the number of bicyclic rings in the molecule. a) Naphthalene ring; b) tetralin ring; c) decalin ring.

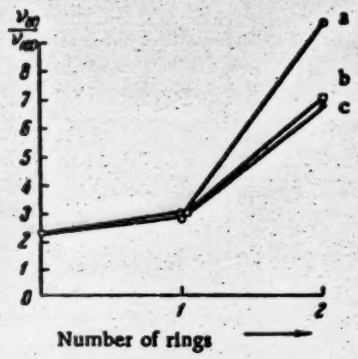
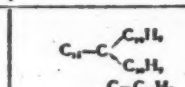
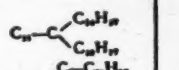
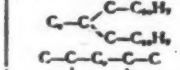
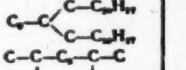
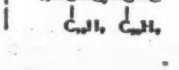
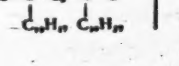


Fig. 2. Variation in viscosity ratio ν_{50}/ν_{100} with the number of condensed bicyclic rings in the molecule. a) Naphthalene ring; b) tetralin ring; c) decalin ring.

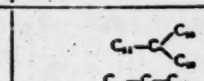
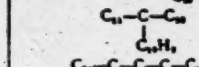
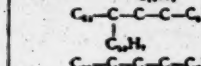
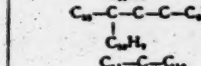
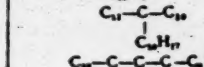
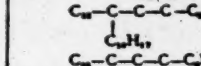
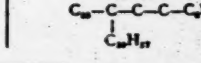
The introduction of naphthalene rings led to a sharper increase in the viscosity than did the introduction of decalin or tetralin rings (Fig. 1). The introduction of the first ring (naphthalene, tetralin, or decalin) into the paraffin hydrocarbon molecule caused little change in the viscosity – temperature curve, increasing its slope only slightly, while the introduction of the second ring led to a sharp increase in the slope of the viscosity – temperature curve. The sharp increase in the slope of the viscosity – temperature curve, particularly in the low-temperature region, is characteristic of hydrocarbons containing two naphthalene rings in the molecule (Table 2 and Fig. 2). The location of the ring in the molecule also has an effect both on the magnitude of the viscosity and on the form of the viscosity – temperature curve. The highest viscosities were possessed by those of the hydrocarbons investigated having a structure in which two naphthalene or decalin rings were attached to the same carbon atom. With the separation of one naphthalene or decalin ring from the other, the viscosity decreased, and in addition the viscosity – temperature curve became flatter (Table 3).

TABLE 3

Expt. No.	Hydrocarbon	ν at 100° (in c. stokes)	$\frac{\nu_{50°}}{\nu_{100°}}$	Expt. No.	Hydrocarbon	ν at 100° (in c. stokes)	$\frac{\nu_{50°}}{\nu_{100°}}$
1		26,40	9,62	1a		19,0	7,13
2		13,55	7,20	2a		16,07	6,05
3		15,10	6,15	3a		16,12	5,18

Of particular interest are the least-studied, complex hybrid structures containing simultaneously naphthalene or decalin rings and cyclohexane or benzene rings. It was found that when a cyclohexane ring was introduced into a molecule containing one naphthalene or decalin ring, the viscosity increased considerably more than when a benzene ring was introduced (Table 4). In addition, the slope of the viscosity – temperature curve also increased.

TABLE 4

Expt. No.	Hydrocarbon	ν at 100° (in centistokes)	$\frac{\nu\ 60°}{\nu\ 100°}$	Increase in viscosity at 100° in %, •	Increase in the ratio $\frac{\nu\ 60}{\nu\ 100}$ %••
1		3,97	2,23	—	—
2		5,58	2,87	140	129
3		6,64	3,34	167	145
4		9,26	3,60	233	160
5		6,33	2,96	159	133
6		7,10	3,22	179	144
7		10,45	3,98	263	178

• The viscosity of hydrocarbon No. 1 was taken as 100% at 100°.

•• The ratio ν_{60}/ν_{100} for hydrocarbon No. 1 was taken as 100%.

LITERATURE CITED

[1] S. R. Sergienko et al, Proc. Acad. Sci. USSR, 120, No. 3, 541 (1958).

[2] R. W. Schiessler and R. D. Clark et al., Petroleum Refiner, 22, 120 (1943).

[3] R. W. Schiessler and C. H. Herr, et al., Proc. Am. Petrol. Inst. Sec. III, 26, 254 (1946).

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SYNTHESIS OF β-[p-DI-(2-CHLOROETHYL)-AMINOPHENYL]-β-ALANINE

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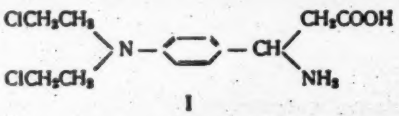
(Presented by Academician M. M. Shemyakin, February 7, 1959)

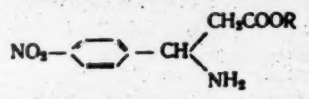
It is well known that p-di-(2-chloroethyl)-amino-β-phenyl-α-alanine ("sarcolysine") possesses high antitumor activity under both experimental and clinical conditions [1, 2]. It seemed to us to be of interest to synthesize and analog of sarcolysine, β-[p-di-(2-chloroethyl)-aminophenyl]-β-alanine (I), a derivative of a β-amino acid.

The starting material for the synthesis of β-[p-di-(2-chloroethyl) -aminophenyl]-β-alanine (I) was β-(p-nitrophenyl)-β-N-acetyl-β-alanine (II), which was prepared by the method of V. M. Rodionov [3].

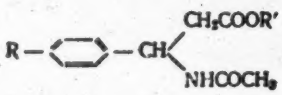
Since the synthesis was the β-amino group blocked by an acetyl radical was accompanied by considerable difficulty and low yields, a second route, in which the β-amino group was blocked with a phthaloyl group, was studied; this method proved to be completely satisfactory.



I

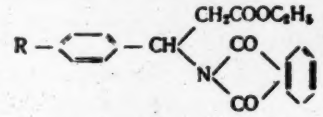


VII R = H



VIII $R = C_2H_5$

II $R = NO_2$, $R' = H$



III $R = NO_2$, $R' = C_2H_5$

IV $R = NH_2$, $R' = C_2H_5$

V $R = (HOCH_2CH_2)_2N$, $R' = C_2H_5$

VI $R = (ClCH_2CH_2)_2N$, $R' = C_2H_5$

IX $R = NO_2$

X $R = NH_2$

XI $R = (HOCH_2CH_2)_2N$

XII $R = (ClCH_2CH_2)_2N$

In the first method, the β-(p-nitrophenyl)-β-N-acetyl-β-alanine (II) was esterified with a 2 N alcoholic solution of hydrogen chloride. The resulting ethyl ester of β-(p-nitrophenyl)-β-N-acetyl-β-alanine [3] (III) smoothly reduced in ethyl alcohol in the presence of skeletal nickel to the ethyl ester of β-(p-aminophenyl)-β-N-acetyl-β-alanine (IV), and the latter was converted to (I) through the following four stages without isolation of the intermediate products in the pure state: the action of ethylene oxide on (IV) in 2 N acetic acid gave the ethyl ester of β-[p-di-(2-hydroxyethyl)-amino-phenyl]-β-N-acetyl-β-alanine (V), and from the latter, by the action of thionyl chloride, was obtained the hydrochloride of the ethyl ester of β-[p-di-(2-chloroethyl)-aminophenyl]-β-N-acetyl-β-alanine [4] (VI). Refluxing of (VI) with 20% HCl gave the hydrochloride of (I), which was then converted to the base (I).

The yield of the final product amounted to 15% of theoretical calculated on the β-(p-aminophenyl)-β-N--acetyl-β-alanine (IV).

In the synthesis by means of the second method, the starting material was the hydrochloride of β-(p-nitrophenyl)-β-alanine (VII) [3], which was esterified by means of an alcoholic solution of hydrogen chloride; the resulting ethyl ester of β-(p-nitrophenyl)-β-alanine (VIII) was smoothly converted by successive treatment with phthalic anhydride and acetic anhydride [5] to the ethyl ester of β-(p-nitrophenyl)-β-N-phthaloyl-β-alanine (IX). Hydrogenation of (IX) in the presence of skeletal nickel gave the ethyl ester of β-(p-aminophenyl)-β-N--phthaloyl-β-alanine (X). Analogously to the conversion of (IV) to (I), and also without isolation of the intermediate products in the pure state, the phthaloyl compound (X) was successively converted to: the ethyl ester of β-(p-di-(2-hydroxyethyl)-aminophenyl)-β-N-phthaloyl-β-alanine (XI) [6], the ethyl ester of β-[p-di-(2-chloroethyl)-aminophenyl]-β-N-phthaloyl-β-alanine (XII), the hydrochloride of (I), and the base (I). The base was obtained in 48% yield calculated on the β-(p-aminophenyl)-β-N-phthaloyl-β-alanine (X).

EXPERIMENTAL

Ethyl ester of β-(p-nitrophenyl)-β-N-acetyl-β-alanine (III). A solution of 10 g (0.04 mole) of β-(p-nitrophenyl)-β-N-acetyl-β-alanine (II) [3] in 100 ml of a 2 N anhydrous alcoholic solution of HCl was refluxed for 1.5 hours, and the alcohol was then completely distilled under vacuum. The residue was extracted with boiling benzene, and the colorless, crystalline precipitate which separated from the benzene solution was filtered off. 7.9 g (70.5%) of (III) was obtained; b.p. 121.5-126°. After recrystallization from alcohol, the material had an m.p. of 125.5-128°. Literature value, 123-124.5° [3].

Ethyl ester of β-(p-aminophenyl)-β-N-acetyl-β-alanine (IV). 6.6 g (0.023 mole) of the ethyl ester of β-(p-nitrophenyl)-β-N-acetyl-β-alanine (III) was hydrogenated at atmospheric pressure in 50 ml of ethyl alcohol in the presence of 5 g of skeletal nickel. The theoretical amount of hydrogen was absorbed during 1.5 hours agitation of the mixture. The alcoholic solution was evaporated under vacuum, and the residue (5.8 g) was ground with 5 ml of ether with heating. 5.3 g (91.2%) of colorless crystals with an m.p. of 72-78° was obtained by filtration. Recrystallization from a mixture of ethyl acetate and benzene gave colorless needles with an m.p. of 79 – 80.5°.

Found %: C 62.15; H 7.48; N 11.53 $C_{13}H_{18}N_2O_3$. Calculated %: C 62.39; H 7.25; N 11.19

The picrate was obtained as yellow crystals, m.p. 155-157° (from alcohol).

Found %: C 47.31; H 4.75; N 14.81 $C_{19}H_{21}N_5O_{10}$. Calculated %: C 47.60; H 4.42; N 14.61

β-[p-di-(2-chloroethyl)-aminophenyl]-β-alanine (I). A mixture of 2.5 g (0.01 mole) of the ethyl esters of β-(p-aminophenyl)-β-N-acetyl-β-alanine (IV), 12 ml of 2 N acetic acid, and 5 ml of ethylene oxide was allowed to stand at room temperature for 42 hours, and the acetic acid and excess ethylene oxide were then distilled under vacuum. To the residue, which was a mobile, yellow oil containing (V), was added 25 ml of dichloroethane; the solvent was partially distilled, and to the well-stirred emulsion, which was cooled with water, was added dropwise, over the course of 7 minutes, 1.9 ml (0.025 mole) of thionyl chloride in 3 ml of dichloroethane. This treatment was accompanied by separation of a yellowish, semisolid mass. The reaction mixture was heated for 45 minutes at 80°, after which the dichloroethane and thionyl chloride were completely distilled under vacuum on a water bath. The residue (VI), a brown mass, was refluxed for 2 hours in 20 ml of 20% hydrochloric acid, and the solution was evaporated under vacuum to a small volume and diluted with 50 ml of water; the flocculent brown precipitate was filtered; the filtrate was treated with activated carbon, and a solution of sodium acetate was added to the solution to precipitate colorless, fine crystals of base (I). The weight of (I) was 0.81 g, m.p. 165-167°. Reprecipitation gave 0.47 g of material with an m.p. of 170-171°. The yield was 15.6% of theoretical. A mixture of this material with (I) obtained from (X) showed no depression of the melting point.

Hydrochloride of the ethyl ester of β-(p-nitrophenyl)-β-alanine (VIII·HCl). A mixture of 27 g (0.109 mole) of the hydrochloride of β-(p-nitrophenyl)-β-alanine [3] and 100 ml of a 2 N solution of HCl in absolute alcohol was refluxed for 3 hours. After the mixture had cooled, 29 g of colorless crystals with an m.p. of 250-251° was filtered. The yield was 97% of theoretical. After recrystallization from alcohol, the material had an m.p. of 251-252°.

Found %: C 48.01; H 5.64; N 10.48; Cl 12.86 $C_{11}H_{15}N_2ClO_4$. Calculated %: C 48.09; H 5.50; N 10.20; Cl 12.90

Ethyl ester of β-(p-nitrophenyl)-β-N-phthaloyl-β-alanine (IX). A solution of 25 g (0.091 mole) of the hydrochloride of the ethyl ester of β-(p-nitrophenyl)-β-alanine, 13.5 g (0.091 mole) of phthalic anhydride, and 45 ml of pyridine was refluxed for 20 minutes; the pyridine was distilled under vacuum, and the residue was refluxed 7 minutes with 45 ml of acetic anhydride. After cooling, the solution was poured into 500 ml of cold water. A yellow oil separated, and this crystallized when ground. Recrystallization from alcohol gave 26.2 g of material with an m.p. of 97-98°. The yield was 78.1% of theoretical. Recrystallization from alcohol gave colorless crystals with an m.p. of 99.5-100.5°.

Found %: C 61.40; H 4.44; N 7.56 $C_{19}H_{16}N_2O_6$. Calculated %: C 61.95; H 4.38; N 7.61

Ethyl ester of β-(p-aminophenyl)-β-N-phthaloyl-β-alanine (X). 25 g (0.068 mole) of the ethyl ester of β-(p-nitrophenyl)-β-N-phthaloyl-β-alanine (IX) was hydrogenated in 180 ml of ethyl alcohol in the presence of 14 g of skeletal nickel; the hydrogenation was carried out at atmospheric pressure and 50.55°. The theoretical amount of hydrogen was absorbed during 1 hour and 10 minutes of agitation. After the mixture was cooled, 20 g of yellow crystals, m.p. 114-115°, was filtered. The yield was 88.3% of theoretical.

Found %: C 67.62; H 5.52; N 8.57 $C_{19}H_{18}N_2O_4$. Calculated %: C 67.44; H 5.36; N 8.28

β-[p-di-(2-chloroethyl)-aminophenyl]-β-alanine (I). A mixture of 2.5 g (0.0074 mole) of the ethyl ester of β-(p-aminophenyl)-β-N-phthaloyl-β-alanine (X), 5 ml of ethylene oxide, and two drops of water was heated in a sealed tube on a water bath for 5 hours. After distillation of the ethylene oxide and water under vacuum, the residue, a yellow oil, was dissolved in 50 ml of chloroform; 35 ml of the solvent was distilled, and 2.5 ml (0.033 mole) of thionyl chloride was added to the residue. Foaming and a slight darkening of the mixture occurred, and the temperature of the reaction mixture rose to 40-45°. The mixture was heated for 10 minutes at 50-54°, and then for 5 minutes at 65-67°. The rapidly darkening brown solution was quickly evaporated under vacuum at a bath temperature of 65-70°. 20 ml of 20% hydrochloric acid was added to the residue, and the mixture was refluxed 1.5 hours; the brown mixture was cooled and diluted with a three-fold volume of water, and the phthalic acid was filtered. When sodium acetate was added to the filtrate, 1.5 g of colorless, finely crystalline base (I) precipitated; m.p. 156-159°. The yield was 67.6% of theoretical.

1.5 g of (I) was dissolved in 6 ml of 20% hydrochloric acid, activated carbon was added, the mixture was diluted with twice its volume of water, and the carbon was filtered; the addition of sodium acetate to the filtrate precipitated 1.08 g of a colorless substance with an m.p. of 176.5-177°. The yield was 48.5%. Reprecipitation gave (I) with an m.p. of 178.5-179°.

Found %: C 50.93; H 6.27; N 8.98; Cl 23.29 $C_{13}H_{18}N_2O_2Cl_2$. Calculated %: C 51.15; H 5.94; N 9.18; Cl 23.24

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INVESTIGATION IN THE FURAN SERIES. SYNTHESIS OF SYMMETRICAL 2, 5-BIS(DIALKYLAMINOMETHYL)FURANS

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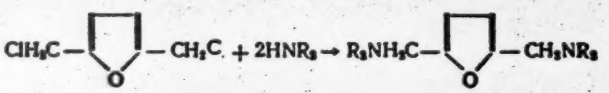
(Presented by Academician A. N. Nesmeyanov, March 5, 1959)

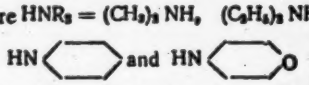
Symmetrical 2, 5-bis(dialkylaminomethyl)furans-[R_2NCH_2-(C_4H_2O)-CH_2NR_2] are almost undescribed in the literature. In 1949, Eliel and Peckham [1], who were studying the applicability of the Mannich reaction to substituted furans, obtained insignificant yields of 2, 5-bis(dimethylaminomethyl)furan by the action of dimethylamine and formaldehyde on N, N-dimethylfurfurylamine in acetic acid; the product was identified as the dipicrate. Diamines of this structure and their quaternary salts are of interest from the point of view of their physiological activity as potential ganglion blocking agents and curarelike compounds. It is well known that the methiodide of 2-dimethylaminomethylfuran (furamon) [2] has found application as a substitute for pilocarpine.

In the synthesis of the symmetrical diamines of the indicated structure we used 2, 5-bis(chloromethyl) furan, the interaction of which with secondary amines led to completely satisfactory yields of the corresponding diamines:



$$ClH_2C-(C_4H_2O)-CH_2Cl + 2HNR_2 \rightarrow R_2NH_2C-(C_4H_2O)-CH_2NR_2$$

where $HNR_2 = (CH_3)_2NH$, $(C_2H_5)_2NH$,



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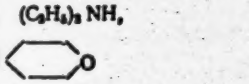

The reaction proceeds readily by the interaction of ether solutions of bis(chloromethyl)furan and the secondary amine in the presence of potassium hydroxide. The secondary amines used in the reaction were dimethylamine, diethylamine, piperidine, and morpholine. In this manner we obtained 2, 5-bis(dimethylaminomethyl) furan, 2, 5-bis(diethylaminomethyl)furan, 2, 5-bis(N-piperidinomethyl)furan, and 2, 5-bis(N-morpholinomethyl) furan. The physical constants of 2, 5-bis(dimethylaminomethyl)furan and its dipicrate were in agreement with the constants of the compounds prepared by another method [1]. It should be pointed out that the dimethiodides of the diamines did not have sharp melting points, and they gradually darkened and then decomposed when heated (in a sealed capillary).

This interaction of 2, 5-bis(chloromethyl)furans with secondary amines is still the only satisfactory method for the preparation of the corresponding symmetrical diamines of the furan series.

EXPERIMENTAL

The 2, 5-bis(chloromethyl)furan was prepared by the method of Moldenhauer and co-workers [3] by the action of thionyl chloride on furfuryl alcohol and subsequent chloromethylation of the furfuryl chloride. The yield of 2, 5-bis(chloromethyl)furan was from 20 to 25%, calculated on the furfuryl alcohol introduced into the reaction. The preparation crystallized in the condenser during distillation from the reaction mixture; m.p. 27-28° (from a mixture of ether and petroleum ether). Literature value: m.p., 27°.

2, 5-Bis(dimethylaminomethyl)furan. A solution of 20 g (0.44 mole) of dimethylamine in absolute ether was placed in a three-necked round-bottom flask fitted with a stirrer, a dropping funnel, and a reflux condenser; 13.4 g of fused KOH was added, and this was followed by the addition, half an hour later, of a solution of 13.2 g (0.08 mole) of 2, 5-bis(chloromethyl)furan in an equal amount of ether; the mixture had to be periodically cooled. After the mixture had stood for 12 hours, water was added until the precipitate completely dissolved, the ether layer was separated, and the water layer was extracted with ether. The combined extracts were dried with fused KOH. After distillation of the ether, vacuum distillation of the residue gave 11.0 g (75.5%) of product: b.p. 76° (2 mm); n_D^{20} 1.4728; d_4^{20} 0.9525; MR_D 53.58. MR_D calculated for $C_{16}H_{18}CN_2\Phi_2$* 54.77.

Found %: C 66.06; 66.17; H 10.07; 10.24 $C_{16}H_{18}ON_2$. Calculated %: C 65.90 H 9.95

The dimethiodide was prepared by the addition of methyl iodide to an alcoholic solution of the diamine; when heated in a sealed capillary, the dimethiodide began to darken at 185° and decomposed at 200-203° (from anhydrous alcohol).

Found %: C 30.40; 30.38; H 5.44; 5.45 $C_{18}H_{24}ON_2I_2$. Calculated %: C 30.92; H 5.19

The dipicrate melted with decomposition at 199-201° (from alcohol).

Found %: N 17.18; 17.12 $C_{22}H_{24}O_{15}N_8$. Calculated %: N 17.50

Literature values: b.p. 107-109° (10 mm); n_D^{20} 1.4728; dipicrate: m.p. 202-205° (with decomposition) [1].

The interaction of 19.8 g (0.12 mole) of 2, 5-bis(chloromethyl)-furan with 50 g of 33% aqueous dimethylamine gave 8.8 g (40%) of 2, 5-bis(dimethylaminomethyl)furan with a b.p. of 81-82° (5 mm).

2, 5-Bis(diethylaminomethyl)furan. From 19.8 g (0.12 mole) of 2, 5-bis(chloromethyl)furan in 20 g of absolute ether and 23.6 g (0.36 mole) of diethylamine in 25 g of ether in the presence of 13.4 g of KOH was obtained, by the method described above, 17.5 g (61%) of product: b.p. 124-126° (7 mm); n_D^{20} 1.4764; d_4^{20} 0.9309. MR_D 72.16. Calculated for $C_{14}H_{26}ON_2\Phi_2$ MR_D 73.24.

Found %: C 70.18; 70.12; H 11.07; 10.96 $C_{14}H_{26}ON_2$. Calculated %: C 70.54; H 10.99

The dimethiodide melted with decomposition at 184-186° (from alcohol).

Found %: C 36.75; 36.59; H 6.29; 6.22 $C_{16}H_{32}ON_2I_2$. Calculated %: C 36.79; H 6.18

Diethiodide: decomposition temperature 208-211° (from alcohol).

Found %: C 39.05; 39.05; H 6.60; 6.81 $C_{18}H_{36}ON_2I_2$. Calculated %: C39.28 H 6.59

Dipicrate: m.p. 127-128° (from alcohol).

Found %: N 15.91; 15.70 $C_{26}H_{32}O_{15}N_8$. Calculated %: N 16.09

2, 5-Bis(N-piperidinomethyl)furan. From 13.2 g (0.08 mole) of bis(chloromethyl)furan in an equal volume of ether and 20.5 g (0.24 mole) of piperidine in the presence of 13.4 g of KOH was obtained, by the method described above, 16.5 g (76.5%) of product: b.p. 172-173° (7 mm); n_D^{20} 1.5130; d_4^{20} 1.0121; MR_D 77.92. Calculated for $C_{16}H_{26}ON_2\Phi_2$ MR_D 78.08.

Found %: C 73.11; 72.96; H 9.85; 10.07 $C_{16}H_{26}ON_2$. Calculated %: C 73.24 H 9.99

Dimethiodide: decomposition temperature 194-198° (from alcohol).

Found %: C39.80; 39.97; H 5.92; 6.01 $C_{18}H_{32}ON_2I_2$. Calculated %: C 39.57 H 5.91

Dipicrate: m.p. 193-194° (from alcohol).

Found %: C 46.74; 46.80; H 4.70; 4.60 $C_{28}H_{32}O_{15}N_8$. Calculated %: C 46.67; H 4.48

2, 5-Bis(N-morpholinomethyl)furan. From 11.5 g (0.07 mole) of 2, 5-bis(chloromethyl)furan and 18.2 g (0.21 mole) of morpholine in ether solution in the presence of 12.5 g of KOH was obtained 11.5 g (62%) of a viscous oil which boiled at 158-160° (1 mm), 181-183° (5 mm); n_D^{20} 1.5198.

Found %: C 62.92; 62.82; H 8.56; 8.47 $C_{14}H_{22}O_3N_2$. Calculated %: C 63.13; H 8.32

* Φ = furan.

Dimethiodide: decomposition temperature 190-193° (from aqueous alcohol).

Found %: C 34.28; 34.14; H 5.38; 5.27 $C_{16}H_{28}O_3N_2I_2$. Calculated %: C 34.92; H 5.13

Dipicrate: m.p. 189-190° (from acetone – alcohol mixture).

Found %: N 15.33; 15.24 $C_{28}H_{28}O_{17}N_8$. Calculated %: N 15.47

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SYNTHESIS OF CYCLIC DIMETHYLSILOXANES CONTAINING TRIETHYLSILOXANE GROUPS

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and N. A. Kurasheva

Cyclic dimethylsiloxane compounds have been synthesized and described a number of times [1-3]. Mixed cyclic compounds containing dimethylsiloxane and alkyl – aryl groups attached to the ring have also been synthesized [4-7].

The present paper describes the synthesis of compounds containing triethylsiloxane groups, compounds of the structure $(C_2H_5)_3SiOSiCl_2$ (R above the second Si) and their conversion by cohydrolysis with dimethyldichlorosilane to cyclic compounds. The synthesis of compounds containing triethylsiloxane groups was carried out according to the reaction [8]

$$(C_2H_5)_3SiONa + RSiCl_3 \rightarrow \underset{R}{Cl_2SiOSi}(C_2H_5)_3 + NaCl.$$

The following compounds were synthesized by means of this reaction: ethyl(triethylsiloxy)dichlorosilane, methyl(triethylsiloxy)dichlorosilane, and phenyl(triethylsiloxy)dichlorosilane. The structure of these compounds was confirmed by analysis and by conversion to acetoxy derivatives according to the reaction

$$R-\underset{Cl}{\overset{Cl}{Si}}-OSi(C_2H_5)_3 + 2CH_3COOK \rightarrow R\underset{OCOCH_3}{\overset{OCOCH_3}{Si}}OSi(C_2H_5)_3 + 2KCl.$$

The properties of these new compounds are presented in Table 1. Cyclic dimethylsiloxanes containing triethylsiloxane groups were prepared by means of cohydrolysis:

$$CH_3SiOSi(C_2H_5)_3 + 5(CH_3)_2SiCl_2 \xrightarrow{H_2O} \text{cyclic } [(CH_3)_2SiO]_5[(CH_3)SiO][OSi(C_2H_5)_3] + 12HCl$$

The cohydrolysis reaction was carried out with an excess of dimethyldichlorosilane in an attempt to introduce the maximum number of dimethylsiloxane groups into the ring; therefore, all experiments were carried out in accordance with the above equation. In a study of the cohydrolysis reaction it was established that during the cohydrolysis of methyl(triethylsiloxy)dichlorosilane with dimethyldichlorosilane, the tetramer – triethylsiloxyheptamethyl-tetrasiloxane – is predominantly formed. The cohydrolysis of ethyl(triethylsiloxy)dichlorosilane

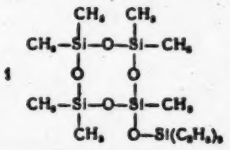
TABLE 1

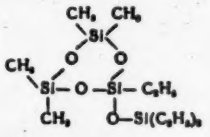
Name of compound	Formula	B.p., °C	n_D^{20}	d_4^{20}	MR_D	
					Calc.	Found
1. Ethyl(triethylsiloxy)-dichlorosilane	$C_2H_5SiOSi(C_2H_5)_3$ (Cl, Cl)	51/2	1,4350	1,0143	66,6	66,5
2. Methyl(triethylsiloxy)-dichlorosilane	$CH_3SiOSi(C_2H_5)_3$ (Cl, Cl)	189,5°	1,4270	1,0079	61,9	62,3
3. Phenyl(triethylsiloxy)-dichlorosilane	$C_6H_5SiOSi(C_2H_5)_3$ (Cl, Cl)	103,5—104,5/3	1,4865	1,0786	82,0	81,6
4. Ethyl(triethylsiloxy)-diacetoxysilane	$C_2H_5SiOSi(C_2H_5)_3$ ($OCOCH_3$, $OCOCH_3$)	91,5/3	1,4217	0,9945	78,4	78,1
5. Methyl(triethylsiloxy)-diacetoxysilane	$CH_3SiOSi(C_2H_5)_3$ ($OCOCH_3$, $OCOCH_3$)	84—86/3	1,4192	0,9972	73,7	73,9
6. Phenyl(triethylsiloxy)-diacetoxysilane	$C_6H_5SiOSi(C_2H_5)_3$ ($OCOCH_3$, $OCOCH_3$)	140/3	1,4696	1,06035	93,8	93,0

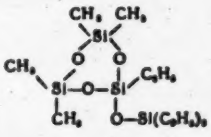
TABLE 2

Name of compound	B.p., °C/mm	d_4^{20}	n_D^{20}	MR_D		Mol. wt.	
				Calc.	Found	Calc.	Found
1. Triethylsiloxyheptamethyltetrasiloxane	88—90/3	0,9629	1,4138	107,4	106,9	412	390
2. Triethylsiloxyethyltetramethyltrisiloxane	109—114/10	0,9554	1,4182	91,7	92,18	350	321
3. Triethylsiloxyphenyltetramethyltrisiloxane	114—120/1	1,0114	1,4548	108,8	107,7	402	394

Structural formulas:

1 

2 

3 

and of phenyl(triethylsiloxy)dichlorosilane with dimethyldichlorosilane leads predominantly to the formation of trimers, namely, triethylsiloxyethyltetramethyltrisiloxane and triethylsiloxyphenyltetramethyltrisiloxane. The properties of these compounds are presented in Table 2. The cyclic structure was confirmed by the analytical data and by the infrared spectra.

1. Synthesis of ethyl(triethylsiloxy)dichlorosilane. 26.6 g (0.163 mole) of ethyltrichlorosilane in 75 ml of C_6H_6 was charged to a three-necked flask fitted with a thermometer, a stirrer, and a reflux condenser, and 25 g (0.163 mole) of the sodium salt of triethylsilanol in 75 ml of C_6H_6 was added, with stirring, over a period of 2 hours at a temperature of 36° in the reaction flask; a precipitate formed during this time. After all of the silanol salt had been added, the mixture was stirred for an additional 3 hours without heating; the precipitate was then filtered, and the filtrate was distilled under reduced pressure. After removal of the benzene at a b.p. of 51°/2 mm, the ethyl(triethylsiloxy)dichlorosilane was separated in a yield of 61.8% of theoretical. n_D^{20} 1.4350; d_4^{20} 1.0143; MR_D found 66.5; calculated 66.6.

Found %: C 37.1; 37.24; H 7.57; 7.69; Si 21.86; 21.80; Cl 27.05; 26.89 $C_8H_{20}Si_2OCl_2$. Calculated %: C 37.1; H 7.73; Si 21.7; Cl 27.4

2. Synthesis of methyl(triethylsiloxy)dichlorosilane. In a similar manner, 8.53 g of methyl(triethylsiloxy)-dichlorosilane was obtained from 16.2 g (0.108 mole) of methyltrichlorosilane and 16.6 g (0.108 mole) of the sodium salt of triethylsilanol in 100 ml of C_6H_6. The yield was 33.2% of theoretical. B.p. 189.5°; n_D^{20} 1.4270; d_4^{20} 1.0079; MR_D found 62.3; calculated 61.9; mol. wt. found 244; calculated 245.

Found %: C 35.30; 35.20; H 7.51; 7.61; Si 22.57; 22.34; Cl 27.83; 28.05 $C_7H_{18}Si_2OCl_2$. Calculated %: C 34.40; H 7.35; Si 22.85; Cl 28.9

3. Synthesis of phenyl(triethylsiloxy)dichlorosilane. 22.54 g of phenyl(triethylsiloxy)dichlorosilane, b.p. 103.5-104.5 deg/3 mm, was obtained in a similar manner from 31.2 g (0.147 mole) of phenyltrichlorosilane and 22.66 g (0.147 mole) of the sodium salt of triethylsilanol in 150 ml of benzene. The yield was 49.8% of theoretical. n_D^{20} 1.4865; d_4^{20} 1.0786; MR_D found 81.6; calculated 82.0; mol. wt. found 302; calculated 307.

Found %: C 46.59; 46.63; H 6.81; 6.71; Si 18.91; 18.70; Cl 23.38; 22.86 $C_{11}H_{18}Si_2OCl_2$. Calculated %: C 46.90; H 6.51; Si 18.24; Cl 23.1

4. Synthesis of ethyl(triethylsiloxy)diacetoxysilane. 25.0 g (0.096 mole) of ethyl(triethylsiloxy)dichlorosilane, 18.9 g (0.192 mole) of anhydrous potassium acetate, and 170 ml of C_6H_6 were charged to a three-necked flask fitted with a stirrer, a thermometer, and a reflux condenser. The mixture was then stirred and heated for 5 hours at 70-80°. The precipitate was filtered, and the filtrate was distilled; after removal of the benzene at 91.5°/3 mm, 14.74 g of ethyl(triethylsiloxy)diacetoxysilane was separated; the yield was 50.0% of theoretical. n_D^{20} 1.4217; d_4^{20} 0.9945; CH_3COO^- found 37.71%; calculated 38.6%; MR_D found 78.1; calculated 78.4.

Found %: C 46.83; 46.87; H 8.54; 8.61; Si 18.54; 18.59 $C_{12}H_{26}Si_2O_5$. Calculated %: C 46.90; H 8.50; Si 18.30

5. Synthesis of methyl(triethylsiloxy)diacetoxysilane. In a similar manner, 5.71 g of methyl(triethylsiloxy)-diacetoxysilane, b.p. 84-86°/3 mm, was obtained from 14.64 g (0.06 mole) of methyl(triethylsiloxy)dichlorosilane and 11.7 g (0.12 mole) of anhydrous potassium acetate in 150 ml of C_6H_6. The yield was 32.8% of theoretical. d_4^{20} 0.9972; n_D^{20} 1.4192; MR_D found 73.9; calculated 73.7; CH_3COO^- found 39.45%; calculated 40.04%.

Found %: C 46.09; 46.23; H 8.55; 8.66; Si 19.39; 19.09 $C_{11}H_{24}Si_2O_5$. Calculated %: C 45.20; H 8.23; Si 19.18

6. Synthesis of phenyl(triethylsiloxy)diacetoxysilane. In a similar manner, 31.44 g of phenyl(triethylsiloxy)-diacetoxysilane, b.p. 140°/3 mm,, was obtained from 34.12 g (0.111 mole) of phenyl(triethylsiloxy)dichlorosilane and 21.8 g (0.222 mole) of anhydrous potassium acetate in 200 ml of C_6H_6. The yield was 79.5% of theoretical. n_D^{20} 1.4696; d_4^{20} 1.06035; MR_D found 93; calculated 93.8; CH_3COO^- found 33.22%; calculated 33.35%.

Found %: C 53.82; 53.60; H 7.45; 7.42; Si 15.84; 16.01 $C_{16}H_{26}Si_2O_5$. Calculated %: C 54.4; H 7.35; Si 15.81

7. Cohydrolysis of dimethyldichlorosilane and ethyl(triethylsiloxy)dichlorosilane. To a three-necked flask fitted with a stirrer, a thermometer, and a reflux condenser were charged 400 ml of H_2O and 200 ml of ether, and then, with vigorous stirring, a mixture of the chlorides, 59.54 g (0.23 mole) of ethyl(triethylsiloxy)dichlorosilane and 150 g (1.16 mole) of dimethyldichlorosilane, was added at ~40°. After the introduction of the chlorides, the mixture was stirred for an additional 3 hours, after which it was washed with water to a negative reaction for chloride ion. The mixture was then dried with anhydrous sodium sulfate. The ether was then evaporated, and the

remaining liquid was distilled at reduced pressure. The fraction, 13.0 g, boiling at 109-114°/10 mm was collected. The yield was 30.06% of theoretical. n_D^{20} 1.4182 d_4^{20} 0.9554 MR_D found 92.18; calculated 91.7; mol. wt. found 321; calculated 352.

Found %: C 40.37; 40.35; H 9.56; 9.61; Si 31.02; 31.38 $C_{12}H_{32}Si_4O_4$. Calculated %: C 40.90; H 9.10; Si 31.8

8. Cohydrolysis of dimethyldichlorosilane and methyl(triethylsiloxy)dichlorosilane. A fraction, 32.02 g, boiling at 88-90°/3 mm was obtained in a similar manner by cohydrolysis of 66.62 g (0.272 mole) of methyl-(triethylsiloxy)dichlorosilane and 176 g (1.360 mole) of dimethyldichlorosilane. The yield was 26.6% of theoretical. n_D^{20} 1.4138; d_4^{20} 0.9629; MR_D found 106.9; calculated 107.4; mol. wt. found 390; calculated 412.

Found %: C 38.28; 38.43; H 8.72; 8.58; Si 33.89; 33.60 $C_{13}H_{36}Si_5O_3$. Calculated %: C 37.9; H 8.72; Si 34.00

9. Cohydrolysis of dimethyldichlorosilane and phenyl(triethylsiloxy)dichlorosilane. A fraction, 34.85 g, boiling at 114-120°/1 mm was obtained in a similar manner by cohydrolysis of 94.2 g (0.307 mole) of phenyl-(triethylsiloxy)dichlorosilane and 198 g (1.53 mole) of dimethyldichlorosilane. The yield was 28.2% of theoretical. n_D^{20} 1.4548; d_4^{20} 1.0114; MR_D found 107.7; calculated 108.8; mol. wt. found 394; calculated 402.

Found %: C 46.36; 46.33; H 8.04; 8.07; Si 28.00; 28.18 $C_{16}H_{32}Si_4O_4$. Calculated %: C 47.7 H 7.96; Si 27.90

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THE ADDITION OF TRIBENZYLSILANE TO OLEFINS

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The study of the addition of silicon hydrides to unsaturated hydrocarbons has recently attracted the attention of a great many investigators. The application of such catalysts as platinized carbon [1], Raney nickel [2], and chloroplatinic acid [3] has significantly extended the possibilities of using this reaction for the synthesis of organosilicon compounds of various structures.

The present work, which is a continuation of our investigations of reactions forming monomeric organosilicon compounds by the addition of silicon hydrides to unsaturated hydrocarbons [4-10], was devoted to a study of addition reactions of tribenzylsilane with olefins. Tribenzylsilane was added to 1-pentene, 1-hexene, 1-octene, 1-nonene, and 1-decene. Chloroplatinic acid was used as the catalyst for the reaction.

By carrying out the reactions at ratios of olefins to tribenzylsilane of 3:1 and 4:1, a reaction time of 2-3 hours, and a temperature of 100-120°, we were able to obtain 50-60% yields of the tribenzylalkylsilanes. These tribenzylalkylsilanes were viscous liquids with high boiling points. The density of the tribenzylsilanes decreased with an increase in the size of the alkyl radical. The densities of tribenzylpentylsilane and tribenzylhexylsilane were greater than unity. The physicochemical properties of the tribenzylalkylsilanes prepared in this work are presented in Table 1.

TABLE 1

Compound	Boiling point		d_4^{20}	n_D^{20}	MR_D	
	°C	mm Hg			calc.	found
$(C_6H_5CH_2)_3SiC_5H_{11}$	205—207	1	1,0161	1,5768	121,52	121,46
$(C_6H_5CH_2)_3SiC_6H_{13}$	253—255	5	1,0023	1,5692	126,15	126,42
$(C_6H_5CH_2)_3SiC_8H_{17}$	259—260	5	0,9903	1,5598	135,41	135,27
$(C_6H_5CH_2)_3SiC_9H_{19}$	260—261	5	0,9857	1,5587	140,04	140,37
$(C_6H_5CH_2)_3SiC_{10}H_{21}$	263—265	5	0,9811	1,5573	144,67	145,20

In order to determine the direction in which the tribenzylsilane adds across the double bond of the olefin, we prepared a number of tribenzylalkylsilanes by an alternate synthesis according to the reaction

$$R\,SiCl_3 + C_6H_5CH_2Li \rightarrow R\,Si\,(CH_2C_6H_5)_3,$$

where R is C_5H_{11}, C_8H_{17}, or C_9H_{19}.

The similarity of the physicochemical properties of the compounds prepared by the addition of tribenzylsilane to olefins to those of the compounds prepared by organolithium synthesis (Table 2) provides a basis for the assumption that the addition of tribenzylsilane to olefins proceeds, under our conditions, contrary to Markovnikov's rule:

$$(C_6H_5CH_2)_3SiH + RCH = CH_2 \rightarrow (C_6H_5CH_2)_3SiCH_2CH_2R.$$

TABLE 2

Product prepared by addition reaction				Compound	Product prepared by organolithium synthesis			
boiling pt.		d_4^{20}	n_D^{20}		boiling pt.		d_4^{20}	n_D^{20}
°C	mm Hg				°C	mm Hg		
253—255	5	1,0023	1,5692	$(C_6H_5CH_2)_3SiC_5H_{11}$	254—255	5	1,5689	1,0019
259—260	5	0,9903	1,5598	$(C_6H_5CH_2)_3SiC_6H_{13}$	258—262	5	1,5604	0,9905
260—261	5	0,9857	1,5587	$(C_6H_5CH_2)_3SiC_9H_{19}$	259—262	5	1,5584	0,9852

EXPERIMENTAL

a) Addition of tribenzylsilane to olefins. The addition of tribenzylsilane to olefins was carried out in a three-necked flask fitted with a stirrer, a reflux condenser, a thermometer, and a dropping funnel. The tribenzylsilane and olefin were placed in the flask and heated, with stirring, to 60°. The (10%) solution of chloroplatinic acid in isopropyl alcohol was then added dropwise. The mixture shortly began to react exothermically. The chloroplatinic acid solution was added at a rate such that the temperature of the reaction mixture did not rise above 100°. The mixture was then heated for 2-3 hours at 100-120°, and finally, fractionated.

The tribenzylsilane was prepared by the interaction of trichlorosilane with benzylmagnesium bromide. 81 g (0.6 mole) of trichlorosilane was added dropwise to the benzylmagnesium bromide, which was prepared from 50 g (2.10 mole) of magnesium and 253 g (2.0 moles) of benzyl chloride. 131 g (74% yield) of tribenzylsilane was obtained. M.p. 89-90° (literature value [10], m.p. 90-91°). The 1-pentene, 1-hexene, 1-octene, 1-nonene, and 1-decene were prepared by pyrolysis of the corresponding acetates at 450-500°; their properties were in agreement with the literature values.

Tribenzylpentylsilane. From 30 g (0.1 mole) of tribenzylsilane and 30 g (0.4 mole) of 1-pentene, in the presence of 1 ml of the chloroplatinic acid solution, was obtained 23.3 g (62.2% yield) of tribenzylpentylsilane. B.p. 205-207° at 1 mm.

Found %: C 83.60; 83.68; H 8.72; 8.68 $C_{26}H_{32}Si$. Calculated %: C 83.87; H 8.60

Tribenzylhexylsilane. From 30 g (0.1 mole) of tribenzylsilane and 33 g (0.4 mole) of 1-hexene, in the presence of 1 ml of the chloroplatinic acid solution, was obtained 19.4 g (51.8% yield) of tribenzylhexylsilane. B.p. 253-255° at 5 mm.

Found %: C 83.90; 83.89; H 8.78; 8.65 $C_{27}H_{34}Si$. Calculated %: C 83.93; H 8.80

Tribenzyloctylsilane. From 30 g (0.1 mole) of tribenzylsilane and 44 g (0.4 mole) of 1-octene, in the presence of 1 ml of the chloroplatinic acid solution was obtained 14.4 g (46.4% yield) of tribenzyloctylsilane. B.p. 259-260° at 5 mm.

Found %: C 83.94; 83.77; H 9.34; 9.40 $C_{29}H_{38}Si$. Calculated %: C 84.06; H 9.13

Tribenzylnonylsilane. From 20 g (0.06 mole) of tribenzylsilane and 25 g (0.2 mole) of 1-nonene, in the presence of 1 ml of the chloroplatinic acid solution, was obtained 12.2 g (43.6% yield) of tribenzylnonylsilane. B.p. 260-261° at 5 mm.

Found %: C 84.13; 84.11; H 9.38; 9.42 $C_{30}H_{40}Si$. Calculated %: C 84.11; H 9.36

Tribenzyldecylsilane. From 30 g (0.1 mole) of tribenzylsilane and 40 g (0.3 mole) of 1-decene, in the presence of 1 ml of the chloroplatinic acid solution, was obtained 27.3 g (62.01% yield) of tribenzyldecylsilane. B.p. 263-265° at 5 mm.

Found %: C 84.14; 83.79; H 9.49; 9.63 $C_{31}H_{42}Si$. Calculated %: C 84.18; H 9.54

b) Preparation of tribenzylalkylsilanes by organolithium synthesis. The alkyltrichlorosilanes were added to the benzyllithium, which was prepared from benzyl chloride and lithium. After distillation of the ether, the reaction mixture was heated at a temperature of 80-100° for a period of 10 hours. After the mixture had cooled,

ether was added, the unreacted lithium was separated, and the reaction mass was decomposed with water. The ether extract was dried with calcium chloride and distilled.

The hexyltrichlorosilane, octyltrichlorosilane, and nonyltrichlorosilane were prepared by addition of trichlorosilane to 1-hexene, 1-octene, and 1-nonene. Benzoyl peroxide was used as the catalyst [7].

Tribenzylhexylsilane. From 5 g (0.7 mole) of lithium, 50 g (0.4 mole) of benzyl chloride, and 24 g (0.1 mole) of hexyltrichlorosilane was obtained 30 g (30.7% yield) of tribenzylhexylsilane.

Tribenzyloctylsilane. From 3.5 g (0.5 mole) of lithium, 40 g (0.3 mole) of benzyl chloride, and 26 g (0.1 mole) of octyltrichlorosilane was obtained 42.7 g (31.0% yield) of tribenzyloctylsilane.

Tribenzylnonylsilane. From 14 g (2 moles) of lithium, 120 g (1 mole) of benzyl chloride, and 79 g (0.3 mole) of nonyltrichlorosilane was obtained 103 g (31.4% yield) of tribenzylnonylsilane.

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FERROCENYLBORIC [FERROCENEBORONIC] AND 1, 1'-FERROCENYLENEDIBORIC [1, 1'-FERROCENEDIBORONIC] ACIDS AND THEIR REACTIONS

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By the action of a mixture of the mono- and dilithium derivatives of ferrocene [1] on n-butyl borate, we were able to obtain a mixture of ferrocenylboric and 1, 1'-ferrocenylenediboric acids [ferroceneboronic and 1, 1'-ferrocenediboronic acids]. These acids were extracted from the reaction mixture with alkali. Separation of the acids was based on the ready solubility in ether of the monoacid and the insolubility of the diboronic acid.

Ferrocenylboric acid is similar in its chemical properties to arylboric acids [areneboronic acids]. Thus, hydrolysis of this acid in the presence of $ZnCl_2$ yields ferrocene; with mercuric chloride, it readily forms ferrocenylmercury chloride, previously described by one of us, É. G. Perevalova and O. A. Nesmeyanova [1], and with cupric chloride and bromide, it yields chloroferrocene and bromoferrocene, the latter having been previously prepared by the cited authors [2] by the action of bromine on diferrocenylmercury. This same route was used to prepare the dihalo derivatives of ferrocene from 1, 1'-ferrocenylenediboric acid.

Thus, there have now become known all three monohalo derivatives of ferrocene – chloro-, bromo-, and iodoferrocene – and all three heteroannular dihaloferrocenes. Moreover, the present work makes it possible to determine the properties of dibromoferrocene with greater accuracy, since the latter can be prepared in a purer, crystalline form through ferrocenylenediboric acid.

It is interesting that ferrocene and biferrocenyl are formed by the interaction of ferrocenylboric acid with an ammoniacal solution of silver oxide, while it is well known that hydrolysis of phenylboric acid [benzeneboronic acid] under the influence of this same reagent yields benzene, but alkylboric acids [alkaneboronic acids] undergo coupling and disproportionation of the radicals.

EXPERIMENTAL

1. Ferrocenylboric and 1, 1'-ferrocenylenediboric acids. The reaction was carried out in a stream of pure, dry nitrogen. An ether solution of 92 g of butyl borate was charged to a flask fitted with a reflux condenser, a stirrer, a dropping funnel, and a tube for the introduction of the nitrogen; the flask was then placed in a dry-ice-acetone bath. The solution was stirred, and an ether solution of ferrocenyllithium was slowly added; the ferrocenyllithium was prepared by metallation of 17.6 g of ferrocene with n-butyllithium (from 39 g of n-butyl chloride and 7.6 g of lithium, about 240 ml total volume of solution). The reaction mixture was stirred until the bath had warmed to room temperature, and was then allowed to stand overnight. The mixture was then decomposed with 10% H_2SO_4. The ether solution was first treated with 40 ml of 10% KOH and then twice with 10-ml portions and five times with 40-ml portions of KOH solution. The alkaline extracts were twice washed with small amounts of ether and acidified with 10% H_2SO_4. The first alkaline extract contained chiefly 1, 1'-ferrocenylenediboric acid. The latter, after acidification of its alkaline solution, was filtered, washed with water to a neutral reaction toward congo indicator, and the still moist material was washed with ether and dried in a vacuum desiccator over 65% H_2SO_4. 2.90 g of 1, 1'-ferrocenylenediboric acid was obtained.

The fourth to eighth alkaline extracts contained almost pure ferrocenylboric acid. After acidification of the extracts, the ferrocenylboric acid was filtered, washed with water to a neutral reaction toward congo indicator, and dried over 65% H_2SO_4. 6.06 g of acid, slightly contaminated with butylboric acid, was obtained.

The second and third alkaline extracts contained a mixture of the mono- and diboric acids. Their separation was based on the ready solubility in ether of the monoboric acid and the insolubility of the diboric acid. The mixture of acids was filtered, washed with water to a neutral reaction toward congo indicator, and dried over 65% H_2SO_4. The mixture was carefully washed with ether, and an additional 0.44 g of 1, 1'-ferrocenylenediboric acid was thereby obtained. Evaporation of the ether gave an additional 0.72 g of ferrocenylboric acid.

The ferrocenylboric acid was recrystallized from water. The over-all yield was 5.50 g (26% of theoretical calculated on the original ferrocene).

Found %: C 52.15; 52.31; H 4.75; 4.94; B 4.70; Fe 24.26 $C_{10}H_{11}FeBO_2$. Calculated %: C 52.24; H 4.92; B 4.71; Fe 24.29

The ferrocenylboric acid was a yellow, crystalline substance which had no sharp melting point, but when it was placed (in a sealed capillary) in a preheated block, it melted at 143-148°; the m.p. changed considerably in dependence on the heating rate. The acid was sparingly soluble in petroleum ether, and was readily soluble in benzene, chloroform, acetone, and alcohols.

The over-all yield of 1, 1'-ferrocenylenediboric acid was 3.34 g (13% of theoretical calculated on the original ferrocene). This acid was recrystallized from water, with large losses.

Found %: C 43.61; 43.67; H 4.64; 4.81; B 7.68; 7.77 $C_{10}H_{12}FeB_2O_4$. Calculated %: C 43.88; H 4.42; B 7.91

1, 1'-Ferrocenylenediboric acid was soluble in alcohols, sparingly soluble in acetone, and insoluble in ether. It decomposed at 180°.

Hydrolysis of ferrocenylboric acid in the presence of $ZnCl_2$. A solution of 0.15 g of $ZnCl_2$ was added to a hot solution of 0.15 g of ferrocenylboric acid in 15 ml of water. The mixture was boiled until the ferrocene had distilled. 0.10 g of ferrocene (82% of theoretical) was obtained; m.p. 168-170°. After recrystallization of the material from methyl alcohol, the m.p. was 172-174°. A mixture with a known sample of ferrocene melted at the same temperature.

1, 1'-Ferrocenylenediboric acid also hydrolyzed to ferrocene under these same conditions.

2. Ferrocenylmercury chloride. An aqueous acetone solution of 0.19g mercuric chloride was added to a hot solution of 0.16 g of ferrocenylboric acid in 20 ml of water. A yellow precipitate immediately formed. The mixture was heated for several minutes, and the ferrocenylmercury chloride was then filtered, washed with water, and dried in a vacuum desiccator over P_2O_5. 0.22 g of ferrocenylmercury chloride (76% of theoretical) was obtained; decomposition temperature, 190-192°. After recrystallization of the material from xylene, the m.p. was 192-194° (with decomposition).

Found %: C 28.52; 28.39; H 2.20; 2.09; Cl 9.04; 8.79; Hg 47.44; 47.44; Fe 13.15; 13.09 $C_{10}H_9FeHgCl$. Calculated %: C 28.52; H 2.15; Cl 8.42; Hg 47.64; Fe 13.26

3. Chloroferrocene. 0.25 g of ferrocenylboric acid in 50 ml of water was placed in a flask fitted with a condenser arranged for distillation, and a solution of 0.30 g of $CuCl_2 \cdot 2H_2O$ in 5 ml of water was added. Chloroferrocene steam-distilled as the reaction mixture was boiled. The chloroferrocene was extracted with ether, and the ether was evaporated; 0.20 g (84% of theoretical) of chloroferrocene, m.p. 53-55°, was obtained, and this material, after recrystallization from alcohol, melted at 59-60°.

Found %: C 54.40; 54.47; H 4.42; 4.30; Cl 16.16; 16.36; Fe 25.27; 25.14 $C_{10}H_9FeCl$. Calculated %: C 54.47; H 4.12; Cl 16.08; Fe 25.33

The chloroferrocene was a yellow, crystalline material which readily dissolved in organic solvents.

Bromoferrocene, 1, 1'-dichloroferrocene, and 1, 1'-dibromoferrocene were obtained in a similar manner; these were yellow, crystalline substances which could be steam-distilled and which were soluble in organic solvents.

4. Bromoferrocene. From 0.16 g of ferrocenylboric acid in 35 ml of water and 0.50 g of cupric bromide in 5 ml of water was obtained 0.15 g (80% of theoretical) of bromoferrocene with an m.p. of 28-30°. After recrystallization of the material from alcohol, the m.p. was 32-33°.

Found %: C 45.53; 45.75; H 3.43; 3.43; Fe 21.04; 20.87; Br 30.11; 29.80 $C_{10}H_9FeBr$. Calculated %: C 45.34; H 3.42; Fe 21.08; Br 30.17

5. 1, 1'-Dichloroferrocene. From 0.50 g of 1, 1'-ferrocenylenediboric acid in 175 ml of water and 3 g of cupric chloride was obtained 0.35 g (75% of theoretical) of 1, 1'-dichloroferrocene with an m.p. of 69-71°. After recrystallization of the material from aqueous alcohol, the melting point was 75-77°.

Found %: C 47.54; 47.33; H 3.22; 3.29; Cl 27.46; 27.63; Fe 21.98; 22.01 $C_{10}H_8FeCl_2$. Calculated %: C 47.12; H 3.16; Cl 27.82; Fe 21.91

6. 1, 1'-Dibromoferrocene. From 1 g of 1, 1'-ferrocenylenediboric acid and 5 g of cupric bromide was obtained 0.95 g (76% of theoretical) of 1, 1'-dibromoferrocene with an m.p. of 42-44°. After recrystallization of the material from alcohol, the m.p. was 50-51°.

Found %: C 35.21; 35.24; H 2.42; 2.43; Fe 16.48; 16.33; Br 45.98 $C_{10}H_8FeBr_2$. Calculated %: C 34.92; H 2.35; Fe 16.24; Br 46.48

7. Interaction of ferrocenylboric acid with an ammoniacal solution of silver oxide. Biferrocenyl. An excess of an ammoniacal solution of silver oxide was added to a solution of 0.60 g of ferrocenylboric acid in water. The reaction mixture was refluxed for several minutes, during which time, metallic silver was precipitated. The reaction mixture was then extracted with ether. The ether was distilled. The residue was dried in a vacuum desiccator over P_2O_5 and petroleum ether was added to it. The ferrocene dissolved in the petroleum ether along with an insignificant amount of biferrocenyl; after repeated washing of the insoluble portion, biferrocenyl was obtained. 0.15 g (31% of theoretical) of ferrocene with an m.p. of 172° was obtained. The biferrocenyl was recrystallized from alcohol. 0.25 g (52% of theoretical) of biferrocenyl with a decomposition temperature of 230° was obtained.

Found %: C 65.10; 65.05; H 5.12; 5.19; Fe 30.07; 30.04 $C_{20}H_{18}Fe_2$. Calculated %: C 64.92; H 4.90; Fe 30.19

The molecular weight was determined: found, 376, 360; calculated for biferrocenyl, 370.

The biferrocenyl was difficultly soluble in petroleum ether and readily soluble in benzene, toluene, dioxane, and tetrahydrofuran.

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BIFERROCENYL

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We have investigated the decomposition of biferrocenylmercury in the presence of palladium black with the aim of preparing biferrocenyl.

Razuvaev and Koton [1] have shown that when organomercury compounds are heated with metal powders in the absence of a solvent, coupling of the radicals takes place. Thus, in the case of diphenylmercury, biphenyl is formed in good yield.

In our case, biferrocenyl was formed only in small yields, and the major product of the reaction was ferrocene;* in addition, a substance insoluble in organic solvents was obtained, probably ferrocene polymer.

TABLE 1

Expt. No.	Amount, g		Heating time, hours	Temp., °C	Yield			
					ferrocene		biferrocenyl	
	Pd	biferrocenylmercury			g	%	g	%
1	1,42	1,5	5 1	170 320	0,36	37	0,06	6,2
2	1	1	5 0,5	250 300	0,24	36	0,04	6,2
3	1	1	5	250	0,30	46	0,03	4,2
4	1	1	29	115	0,11	16,5	0,01	1,5
5	1,3	2,69	5	250	0,87	49	0,11	6,3
6	0,79	2,37	5	250	0,60	40	0,05	3,5

The appearance of ferrocene in this reaction apparently can be explained only by disproportionation of the intermediately formed ferrocenyl radicals with the formation of ferrocene and ferrocene polymers or biferrocenyl.

$$2\,(C_5H_5FeC_5H_4)_2Hg \xrightarrow{Pd} 4C_5H_5FeC_5H_4^{\cdot} + 2Hg$$

$$4\,C_5H_5FeC_5H_4^{\cdot} \rightarrow 2\,(C_5H_5)_2Fe + \underset{\underset{C_5H_4-C_5H_4}{Fe}}{\overset{C_5H_4-C_5H_4}{Fe}}$$

In a series of experiments (carried out in sealed tubes and without a solvent) in which the temperature conditions and amounts of catalyst were varied, the yield of ferrocene and biferrocenyl varied, respectively, from

* We have previously observed the formation of ferrocene during exchange reactions of ferrocene derivatives in a medium of hydrogen-containing solvent [2, 3].

16 to 49% and from 1.5 to 6.3% (see Table 1). The ferrocene and biferrocenyl were separated from each other by chromatography on aluminum oxide; the first was eluted with petroleum ether, and the second was eluted with a mixture (2:1) of petroleum ether and benzene.

The presence of ferrocene polymers in the reaction products was shown as follows. The residue remaining after treatment of the reaction mixture with organic solvents (including hot xylene for removal of the diferrocenylmercury) contained, judging from its weight, not only palladium and mercury formed as a result of the reaction, but also an organic portion, and the weight of this portion was equal to the weight of the ferrocene formed (as would follow from the equation presented above for the reaction). Analysis of the insoluble residue for carbon and hydrogen gave the same carbon–hydrogen ratio as in biferrocenylene or ferrocene polymer.

The biferrocenyl was an orange, crystalline substance, readily soluble in benzene and less soluble in petroleum ether, ether, and alcohol; it was crystallized from alcohol.

Found %: C 64.97; 65.16; H 5.07; 5.25; Fe 29.59; 29.83 $C_{20}H_{18}Fe_2$. Calculated %: C 64.91; H 4.91; Fe 30.18

The biferrocenyl was less thermally stable than ferrocene. When heated, it began to darken at 205°, and it melted with partial decomposition at about 230°; however, ferrocene was not formed during the decomposition, as was shown by special experiments. Thus, when biferrocenyl was heated in a sealed tube at 250° for 5 hours, 80% of the original biferrocenyl was recovered. Ferrocene was not detected in the decomposition products. Consequently, the ferrocene produced during the catalytic cleavage of diferrocenylmercury was not a product of the thermal decomposition of biferrocenyl.

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SYNTHESIS OF ORGANOSILICON MONOMERS FROM DICHLOROSILANE

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The high reactivity of methyl- and ethyldichlorosilanes in catalytic addition reactions to unsaturated compounds, which we have previously observed [1, 2], provides a basis for the assumption that dichlorosilane, for which the steric effect of substituents is reduced to a minimum in comparison to alkyldichlorosilanes, would be a very reactive compound in reactions of the first Si—H bond.

In addition, the study of conversions of dichlorosilane has given promise of the discovery of new possibilities of both theoretical and practical interest. The only methods described in the literature for the use of dichlorosilane in the synthesis of phenylchlorosilanes [3] involve the thermal or catalytic condensation of dichlorosilane with benzene at high temperatures (300-500°) and pressures (70-280 atm.). Dichlorosilane has also been used for the synthesis of trifluoropropyl- and di(trifluoropropyl)dichlorosilanes by addition to trifluoropropylene under the influence of ultraviolet light [4]. Although these reactions provide interesting monomers, their broad application as preparative methods is attended by a number of difficulties connected with the necessity of working at high pressures and with pure compounds free from inhibitors of radical reactions as well as other limitations.

The presence of two Si—H bonds in dichlorosilane would lead one to expect the formation of two series of compounds—$RSiHCl_2$ and R_2SiCl_2. During investigations of the thermal condensation of dichlorosilane with C_6H_5Cl and $CH_2 = CHCl$ and of the catalytic addition of dichlorosilane to unsaturated compounds, we observed the formation of both $RSiHCl_2$ and R_2SiCl_2 depending on the conditions under which the experiments were carried out. Compounds of the type $RSiHCl_2$, particularly $C_6H_5SiHCl_2$, were of particular interest to us, since they opened up a new route for the synthesis of new monomers of the structure $RR'SiCl_2$, particularly fluorine-containing monomers, in which the radicals attached to the silicon atom are different. In spite of the rather harsh temperature conditions (600-680°), phenyldichlorosilane is the major product, and is obtained as a mixture with phenyltrichlorosilane and diphenyldichlorosilane. Under the conditions investigated, the over-all yield of phenylchlorosilanes amounted to 50% of theoretical (77-83% of the H_2SiCl_2 reacted). The results of our experiments are presented in Table 1.

Dichlorosilane also undergoes thermal condensation with vinyl chloride at temperatures of 535-545° C. The only positively identified reaction product was vinyldichlorosilane, which was obtained in 20% yield. The formation of a mixture of high-boiling reaction products indicates the complex nature of the reaction of dichlorosilane with vinyl chloride. Thus, that it is possible to obtain silanes of the type $RSiHCl_2$ from dichlorosilane and RCl, even under harsh temperature conditions, has been demonstrated, and this substantially extends the possibilities of thermal condensation reactions [5]. As experiments with ethylene and propylene showed, the addition of dichlorosilane to unsaturated compounds in the presence of H_2PtCl_6 can also be directed, to a considerable extent, toward the formation of compounds to the type $RSiHCl_2$ (see Table 2). Thus, in the reaction with ethylene, the yield of $C_2H_5SiHCl_2$ was 42% of theoretical. The over-all yield of compounds of the types $RSiHCl_2$ and R_2SiCl_2 under these conditions was almost quantitative. The use of an excess of the unsaturated compound led to the formation of only dialkyldichlorosilanes—R_2SiCl_2. Moreover, besides addition of H_2SiCl_2 to the simplest olefins (ethylene and propylene), the addition to more complex saturated compounds, for example, the fluorinated ether $-CH_2 = CHCH_2OCF_2CFClH$, was also studied. These experiments have established the preparation of alkyldichlorosilanes of the type $RSiHCl_2$ from H_2SiCl_2 as an important method for the synthesis of monomers of this type. The

TABLE 1

Thermal Condensation of H_2SiCl_2 with C_6H_5Cl

Ratio Cl_2SiH_2 / C_6H_5Cl in g (mole)	Duration of experiment, hours	Temperature in reaction zone, °C	Amount of condensate, g	Distillation products, grams: Cl_2SiH_2	$ClSiH_3$	C_6H_6	C_6H_5Cl	$C_6H_5SiCl_2H$	$(C_6H_5)_2SiCl_2$	$C_6H_5SiCl_3$	Yield, % of theor. calc. on H_2SiCl_2: $C_6H_5SiCl_2H$	$(C_6H_5)_2SiCl_2$	$C_6H_5SiCl_3$	Over-all yld. of phenylchlorosilanes, % of theor. calc. on H_2SiCl_2	Over-all yld. of phenylchlorosilanes calc. on H_2SiCl_2 fed, %	Ratio of diameter to length of tube, mm
30,5 (0,3) / 39,5 (0,35)	2,5	630÷63[illegible]	65,5	10,5	2,0	2,0	21,0	12,5	6,0	—	24,0	8,0	—	32,0	49,0	20/600
40,5 (0,4) / 47,5 (0,42)	2,5	660÷68[illegible]	[illegible]2	8,0	6,0	9,0*	13,5	17,0	5,2	8,5	24,5	5,0	10,0	39,5	49,0	20/600
30,5 (0,3) / 39,5 (0,35)	3,0	618÷623	67	12,5	2,0	4,5	22,0	14,0	3,5	—	26,5	4,5	—	31,0	52,5	24/600
50,5 (0,5) / 112,6 (1)	4,0	660÷680	159	18,0	5,0	18,5*	35,0	18,3	10,2	26,0	21,0	8,0	25,0	54,0	83,0	17/600
25,5 (0,25) / 66 (0,6)	5,0	636÷638	85,5	8,0	3,5	8,0*	32,0	11,0	6,5	10,0	24,5	10,0	18,5	53,0	77,0	24/600

* A very small amount of biphenyl was also formed in these experiments.

TABLE 2

Addition of H_2SiCl_2, $C_6H_5SiHCl_2$, and $p\text{-}FC_6H_4SiHCl_2$ to Unsaturated Compounds in The Presence of an 0.1 M Solution of $H_2PtCl_6 \cdot 6H_2O$ in Isopropyl Alcohol

Expt. No.	Starting Materials	Amt. in g (moles)	Amt. of H_2PtCl_6, ml	React. temp., °C	Max. press., atm.	React. time, hours	Wt. react. prod., g	Addition products	Yield: yield in g	Yield: % theoret.
1	Cl_2SiH_2 / $CH_2=CH_2$	20 (0,2) / 5,6 (0,2)	0,1	20	15	0,25	25	$C_6H_5SiCl_2H$ / $(C_6H_5)_2SiCl_2$	10,8 / 8,0	42,0 / 25,5
2	Cl_2SiH_2 / $CH_2=CH_2$	18 (0,18) / 10 (0,36)	0,05	20	15	0,34	26	$(C_6H_5)_2SiCl_2$	22,0	79,0
3	Cl_2SiH_2 / $CH_2=CHCH_3$	18,2 (0,18) / 7,6 (0,18)	0,15	20	7	0,5	25,6	$C_6H_5SiCl_2H$	15,5	60,5
4	Cl_2SiH_2 / $CH_2=CHCH_3$	16,2 (0,16) / 13,5 (0,32)	0,1	20	7	1,5	30,0	$(C_6H_5)_2SiCl_2$	20,5	69,0
5	Cl_2SiH_2 / $CH_2=CHCH_2OCF_2CFClH$	14,3 (0,14) / 21 (0,12)	0,15	88	5,5	1,5	32,5	$Cl_2SiCH_2CH_2CH_2OCF_2CFClH$	14,0	42,0
6	Cl_2SiH_2 / $CH_2=CHCH_2OCF_2CFClH$	10,1 (0,10) / 35 (0,2)	0,1	75	3,0	2,0	46,0	$Cl_2Si(CH_2CH_2CH_2OCF_2CFClH)_2$	20,0	44,5
7	$C_6H_5SiCl_2H$ / $CH_2=CHCF_3$	17,8 (0,1) / 9,7 (0,1)	0,2	97	15,0	2,0	25,6	$C_6H_5SiCl_2CH_2CH_2CF_3$	19,0	69,5
8	$p\text{-}FC_6H_4SiCl_2H$ / $CH_2=CHCF_3$	17,5 (0,09) / 8 (0,08)	0,2	144	11,0	2,5	20,0	$p\text{-}FC_6H_4SiCl_2CH_2CH_2CF_3$	4,5	17,0

reaction of H_2SiCl_2 with acetylene proceeds in a more complex manner. Polymeric products containing the unit

$$-SiCl_2CH_2CH_2-SiCl_2-$$

are formed. Under the conditions, investigated, we were unable to obtain vinyl- and divinyldichlorosilanes by this method. We always obtained a mixture of high-boiling liquid and solid polymers.

TABLE 3

Expt. No.	Compound	B.p., °C (mm Hg)	d_4^{20}	n_D^{20}	MR found	MR calc.
1	$C_6H_5SiCl_2H$	181,5 (750)	1,2115	1,5257	44,85	44,84
2	$C_6H_5SiCl_3$	200,8 (746)	1,3210	1,5208	48,99	48,84
3	$(C_6H_5)_2SiCl_2$	141—141,5 (5)	1,2216	1,5819	69,16	68,88
4	$CH_2=CHSiCl_2H$	65,2 (746)	1,1214	1,4254	29,00	29,33
5	$Cl_2Si(H)CH_2CH_2CH_2OCF_2CFH$•	188 (746)	1,3886	1,4171	49,22	50,39
6	$Cl_2Si(CH_2CH_2CH_2OCF_2CFH)_2$•	151—152 (6)	1,4296	1,4240	80,36	79,99
7	p-$FC_6H_4SiCl_2H$•	177 (747)	1,2936	1,5030	44,59	44,87
8	$C_6H_5Si(Cl_2)CH_2CH_2CF_3$•	99—100 (10)	1,3048	1,4737	50,80	50,56
9	p-$FC_6H_4Si(Cl_2)CH_2CH_2CF_3$•	101—103 (10)	1,3641	1,4645	58,95	58,95
10	$(F_3CCH_2CH_2)_2SiCl_2$	162 7.92	1,3643	1,3810	49,16	49,34

• These substances were prepared for the first time in the present work.

Phenyldichlorosilane, prepared by thermal condensation of H_2SiCl_2 with C_6H_5Cl, and also $FC_6H_4SiHCl_2$ gave good yields of the addition products when reacted with $CH_2=CHCF_3$ in the presence of chloroplatinic acid (Table 2). Some of the physical properties of the compounds obtained in this work are presented in Table 3.

EXPERIMENTAL

1. Preparation of dichlorosilane. H_2SiCl_2 was prepared by disproportionation of $HSiCl_3$• in the presence of dimethylcyanamide [6]. 250 g of $HSiCl_3$ and 11 g of activated dimethylcyanamide were charged to the kettle of a rectification column packed with nichrome packing (~35-40 theoretical plates). The H_2SiCl_2 was taken overhead continuously and condensed in a trap cooled with solid CO_2 and acetone. The reaction time was about 6-7 hours. The other reaction products ($HSiCl_3$ and $SiCl_4$) were then distilled from this same flask. A new portion of $HSiCl_3$ was added to the residue which contained the catalyst and some $SiCl_4$, and the reaction was continued precisely as described above. The yield of H_2SiCl_2 varied from 50 to 70% of theoretical. There was almost no loss of catalyst activity during 15 experiments. A total of 850 g of H_2SiCl_2 (b.p. +8-9° at 745 mm) was obtained by this method from 3000 g of $HSiCl_3$.

2. Preparation of phenylchlorosilanes. The conditions and results of the experiments on the synthesis of phenyldichlorosilanes by thermal condensation of dichlorosilane (H_2SiCl_2) with chlorobenzene are presented in Table 1. Some of the physical constants of the compounds obtained are presented in Table 3.

3. Synthesis of vinyldichlorosilane. The glass reaction tube, which had an internal diameter of 20 mm and a reaction-zone length of 600 mm, was heated to 535-545°, and a mixture of 30.5 g (0.3 mole) of H_2SiCl_2 and 41.5 g (0.66 mole) of $CH_2=CHCl$ was passed through the tube over a period of 4.5 hours.•• Fractionation of the resulting condensate gave 7.8 g (20%) of $CH_2=CHSiHCl_2$, b.p. 65.2° (746 mm); d_4^{20} 1.1214; n_D^{20} 1.4254; MR found; 29.00 MR calculated; 29.33.

4. Addition of H_2SiCl_2, $C_6H_5SiHCl_2$, and p-$FC_6H_4SiHCl_2$ to unsaturated compounds. The conditions and results of all experiments on the catalytic addition of dichlorosilane, phenyldichlorosilane, and p-fluorophenyldichlorosilane to unsaturated compounds in the presence of H_2PtCl_6 are presented in Table 2, and some of the physical constants of the resulting products are presented in Table 3.

5. Synthesis of p-fluorophenyldichlorosilane, p-$FC_6H_4SiHCl_2$. A solution of 95 g (0.7 mole) of trichlorosilane ($HSiCl_3$) in 100 ml of absolute ether was placed in a three-necked flask fitted with a mechanical stirrer, a reflux condenser, and a dropping funnel, and p-FC_6H_4MgBr, prepared from 17 g (0.7 g atom) of Mg and 98 g (0.56 mole) of p-FC_6H_4Br in 400 ml of absolute ether, was added with vigorous stirring. The reaction mixture was heated for two hours. After separation of the precipitate, distillation of the ether, and distillation in a column, there was obtained 21.1 g (19%) of p-$FC_6H_4SiHCl_2$; b.p. 177° (747 mm), d_4^{20} 1.2936, n_D^{20} 1.5030. MR found; 44.59 MR calculated; 44.87.

• A mixture of $HSiCl_3$ and $SiCl_4$, for example, a mixture containing 95% $HSiCl_3$ and 5% $SiCl_4$, can also be used in this reaction.

•• In all thermal-condensation experiments, the system was purged with nitrogen at the beginning and end of each experiment.

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A NEW SYNTHESIS OF β-IONOLIDENEACETALDEHYDE

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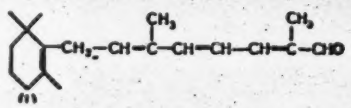
9, 13-dimethyl-7-(1, 1, 5-trimethylcyclohexen-6-yl)-8, 10, 12-octatrien-14-al, a C_{19} aldehyde (I), is an intermediate product in the synthesis of β-carotene [1].

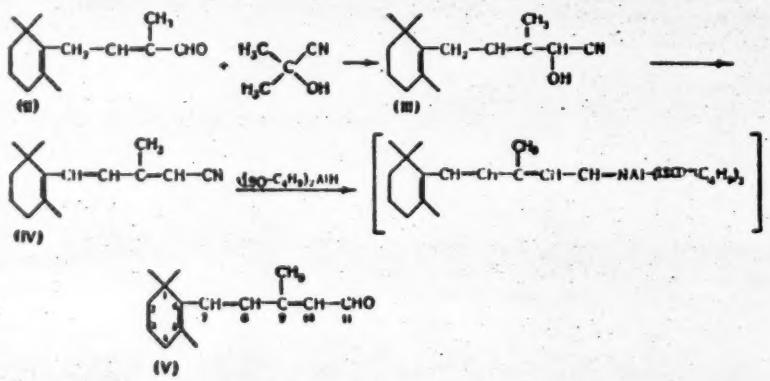


(I)

Lengthening of the carbon chain of this compound by one atom and creation of a system of conjugated double bonds converts this aldehyde to one of the stereoisomeric retinals – the aldehyde corresponding to vitamin A.

One method for lengthening the chain by one carbon atom involves the preparation of the cyanohydrin [2, 3]. Reduction of the nitrile resulting from dehydration of the cyanohydrin can be accomplished through the use of diisobutylaluminum hydride [4].

The present paper describes the use of this method for a simpler synthesis – the synthesis of β-ionolidene-acetaldehyde [5] from 7-(1, 1, 5-trimethylcyclohexen-6-yl)-9-methyl-8-buten-10-al, a β-C_{14} aldehyde (II), according to the scheme



The interaction of C_{14} aldehyde (II) with acetone cyanohydrin proceeded at 20-23° under the influence of a methanol solution of potassium carbonate; the yield of hydroxynitrile (III) was 83-84%. The dehydration was carried out by means of phosphoryl chloride and pyridine [6]. The β-ionolideneacetonitrile (IV) was separated by vacuum fractionation. Its optical properties (Figure 1) were in good agreement with those described in the literature [7] for β-ionolideneacetonitrile prepared by the condensation of β-ionone with cyanoacetic acid. Reduction of nitrile (IV) with diisobutylaluminum hydride was carried out in benzene solution at 0° with a gradual increase in the temperature. The resulting aldimine was hydrolyzed with dilute acid, and the β-ionolideneacetaldehyde (V) was isolated as a mixture of its stereoisomers. By crystallization of the semicarbazones of the stereoisomeric aldehydes from alcohol, the semicarbazone of trans-β-ionolideneacetaldehyde, m.p. 195.5-196° [7, 8], and, in considerably smaller amount, the semicarbazone of the cis isomer, m.p. 173-174°, were obtained. The ultraviolet absorption spectra of the semicarbazones of these isomeric aldehydes were in close agreement with respect to location of the absorption maxima (λ_{max} 318 and 312 mμ, respectively) (Fig. 2). This indicates that the isomerism is due to different distribution of the substituents with respect to the newly formed, sterically unhindered double bond between carbon atoms 9 and 10.

The free aldehyde was obtained from the semicarbazone of trans-β-ionolideneacetaldehyde; its infrared transmission spectrum (Fig. 3) showed an intense band at 10.3μ corresponding to the deformation vibration of the hydrogen atoms outside the plane of the double bond, which is characteristic for substances with a trans disposition of substituents across a double bond. The spectrum had a band in the region of 6.25μ, which is related to vibration of the system of conjugated double bonds, and one at 6μ corresponding to an unsymmetrical valence vibration ν C = O in a system with conjugated multiple bonds.

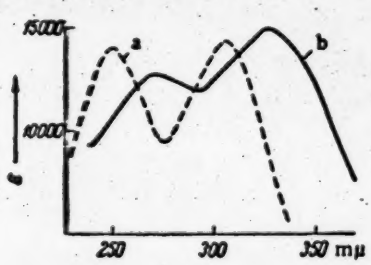


Fig. 1. Ultraviolet absorption spectra; a) β-ionolideneacetonitrile, b) β-ionolideneacetaldehyde.

The authors express their deep appreciation to Prof. N. A. Preobrazhenskii for his attention to and interest in this work.

EXPERIMENTAL

7-(1, 1, 5-trimethylcyclohexen-6-yl)-9-methyl-8-buten-10-al cyanohydrin (III). A mixture of 13 g of the C_{14} aldehyde (n_D^{20} 1.5113), 0.72 g of freshly prepared acetone cyanohydrin, and 11 ml of a 3% solution of potassium carbonate in methanol was allowed to stand at 20-23° in an atmosphere of nitrogen for 120 hours. The reaction mixture was dissolved in 70 ml of petroleum ether (b.p. 40-70°) and extracted with methanol. The combined methanol extracts were agitated with a small amount of petroleum ether (20 ml) to remove traces of the C_{14} aldehyde, diluted with a threefold amount of water, and extracted with ether. The ether extract was washed with a solution of sodium bicarbonate and dried with magnesium sulfate. After evaporation of the solvent and heating at 1-2 mm to 40-45°, 12.5 g, 85.3%, of the C_{14} aldehyde cyanohydrin was obtained as an oily substance.

Found %: active hydrogen 0.428; N 6.24; 6.19 $C_{15}H_{23}ON$. Calculated %: active hydrogen 0.429; N 6.003

β-Ionolideneacetonitrile (IV). A solution of 17.48 g of C_{14} aldehyde cyanohydrin in 13.6 ml of dry pyridine was added, over a period of 15 minutes and with stirring, to a freshly distilled mixture of 13.6 ml of phosphoryl chloride and 54.4 ml of dry pyridine; nitrogen was passed through the reaction mixture during introduction of the cyanohydrin. With the first introduction of the cyanohydrin, the temperature increased to 60-70°. Stirring was continued for 3 hours at the boiling point (116-120°), and the reaction mixture was then cooled, poured onto crushed ice (300 g), and extracted with ether. The extract was washed with 5% H_2SO_4 and a solution of sodium bicarbonate, and dried with $MgSO_4$; the solvent was evaporated, and the residue (10.1 g) of raw C_{15} nitrile was fractionated. 8.38 g, 52.1%, of β-ionolideneacetonitrile was obtained as a greenish yellow oil; b.p. 121-125° (in the bath), 0.03 mm; d_4^{20} 0.9635; n_D^{20} 1.5523.

Found %: C 83.50; H 9.88; N 6.32 $C_{15}H_{21}N$. Calculated %: C 83.67; H 9.83; N 6.50

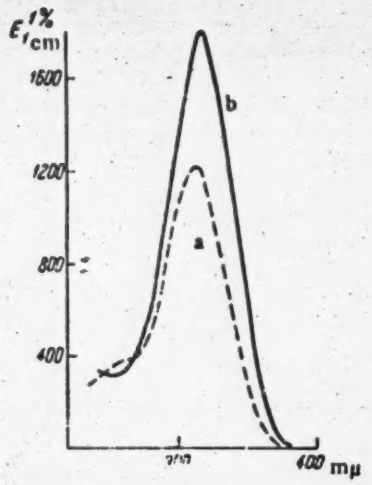


Fig. 2. Ultraviolet absorption spectra. Semicarbazones of β-ionolideneacetaldehydes: a) cis, b) trans.

The material had two absorption maxima, $E_{305m\mu}$ 14400; $E_{250m\mu}$ 14280, in ethanol (Fig. 1).

β-Ionolideneacetaldehyde (V). A solution of 6 g of β-ionolideneacetonitrile in 18 ml of dry benzene was cooled to 0°, and a solution of 4.4 g of diisobutylaluminum hydride in 11 ml of dry benzene was added dropwise, with stirring, over a period of 1 hour and 15 minutes; the addition was carried out in an atmosphere of dry nitrogen. With the first addition of the hydride, the temperature of the reaction mixture increased from 0 to 32°. Stirring was continued for another 3 hours at 35-40° after completion of the addition of the solution of hydride. The reaction mixture was cooled and poured, with stirring, into 50 ml of water at 8-12°, and stirring was continued for another 10 minutes. In order to complete the decomposition of the aldimine intermediate, 30 ml of 10% H_2SO_4 was added, at 0°, to the gelatinous reaction mixture, the mixture was heated to 30°, and stirring was continued for 10 minutes. The benzene layer was separated, and the aqueous layer was extracted with benzene. The benzene extract was washed with a solution of sodium bicarbonate and dried with $MgSO_4$. The solvent was evaporated, and the residue (5.86 g; 97.3%), a reddish oil, n_D^{20} 1.5643, was distilled. The fraction distilling at 165-175° (in the bath) at 0.02 mm was collected. There was obtained 3.35 g, 55.7%, of a yellowish oil with the characteristic ultraviolet absorption spectrum $E^{1\%}_{1cm}$ 720 (320 mμ), $E^{1\%}_{1cm}$ 627 (267 mμ), in ethanol.

Semicarbazone of trans-β-ionolideneacetaldehyde. 2.6 g of the raw β-ionolideneacetaldehyde was dissolved in 5.2 ml of ethanol, and the solution was mixed with a solution of 2 g of semicarbazide base in 6.2 ml of 50% alcohol. The reaction mixture was allowed to stand at 20° for 3 hours and then at 0° for a day. The raw semicarbazone, 2.14 g, 65.3%, was recrystallized from 32 ml of methanol; 1.385 g trans-β-ionolideneacetaldehyde semicarbazone was obtained as lustrous, prismatic yellow crystals. M.p. 195.5-196°; $E^{1\%}_{1cm}$ 1816 (318 mμ).

Found %: C 69.93; H 9.24; N 15.24 $C_{16}H_{25}ON_3$. Calculated %: C 69.73; H 9.08; N 15.26

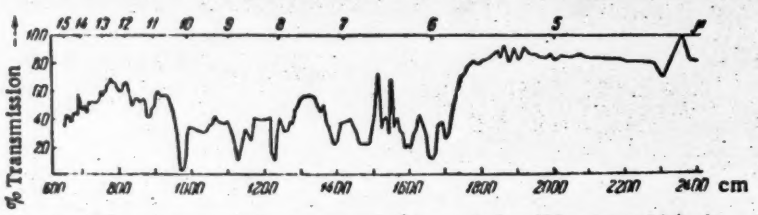


Fig. 3. Infrared transmission spectrum of trans-β-ionolideneacetaldehyde.

Semicarbazone of cis-β-ionolideneacetaldehyde. The mother liquor obtained from the separation of the trans-β-ionolideneacetaldehyde semicarbazone was allowed to stand at 0° for 4-5 days, during which time lustrous, acicular crystals precipitated in clusters (0.33 g). Recrystallization from dry benzene (1.5 ml) and methanol (0.8 ml) gave 0.12 g of cis-β-ionolideneacetaldehyde semicarbazone in the form of lustrous yellow crystals; m.p. 173-174°. (A mixture with a known sample of trans-β-ionolideneacetaldehyde semicarbazone melted at 158-166°) $E^{1\%}_{1cm}$ 1230 (312 mμ) in ethanol. An additional 0.11 g of cis-β-ionolideneacetaldehyde was obtained from the mother liquor.

Found %: C 69.91; H 9.09; N 15.20 $C_{16}H_{25}ON_3$. Calculated %: C 69.73; H 9.08; N 15.26

Trans-β-ionolideneacetaldehyde. 1.2 g of trans-β-ionolideneacetaldehyde semicarbazone (m.p. 195.5-196°) was dissolved in 60 ml of CH_3COOH, 0.6 g of pyroracemic acid was added, and the mixture was heated to boiling in a stream of nitrogen over a period of 40 minutes. After the solution had cooled, it was diluted with water and extracted with petroleum ether. The solution was washed with a saturated solution of sodium bicarbonate and dried with $MgSO_4$; the solvent was removed, and the residue (0.7 g) was dissolved in 5 ml of petroleum ether (40-70°) and chromatographed on 12 g of aluminum oxide (activity III). Elution with petroleum ether (40-70°) containing 5% ether gave 60 ml of eluent, from which was obtained 0.32 g, 33.6%, of the aldehyde as an oily material with the characteristic absorption spectrum, $E^{1\%}_{1cm}$ 691 (326 mμ), 584 (270 mμ), in ethanol.

Found %: C 82.55; H 9.50 $C_{13}H_{22}O$. Calculated %: C 82.44; H 10.16

The infrared spectrum in the region 16-4μ was taken with an IKS-11 spectrometer with an NaCl prism at a layer thickness of 54μ.

The authors express their appreciation to L. V. Luk'yanova for taking the infrared spectra and for aiding in their interpretation.

β-Ionolideneacetaldehyde 2, 4-dinitrophenylhydrazone. A hot solution of 0.4 g of 2, 4-dinitrophenylhydrazine hydrochloride in 40 ml of absolute C_2H_5OH containing 0.4 ml of concentrated HCl was added to a solution of 0.4 g of the raw β-ionolideneacetaldehyde in 2 ml of ethanol. The reaction mixture was allowed to stand overnight, and dark red crystals (0.6 g) separated. Recrystallization from methanol gave 0.41 g, 56.3%, of β-ionolideneacetaldehyde 2, 4-dinitrophenylhydrazone in the form of gold-cherry crystals.

M. p. 198-199°; $E^{1\%}_{1cm}$ 1440 (410 mμ), 628 (316 mμ), 628 (255 mμ), in ethanol.

Found %: C 63.18; H 6.67; N 14.37 $C_{21}H_{28}O_4N_4$. Calculated %: C 63.30; H 6.58; N 14.06

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STEREOCHEMISTRY OF HETEROCYCLIC COMPOUNDS. CONFIGURATIONS OF THE GEOMETRIC ISOMERS OF 1,2,5--TRIMETHYL-4-PHENYL-4-PIPERIDOLS

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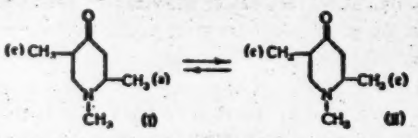
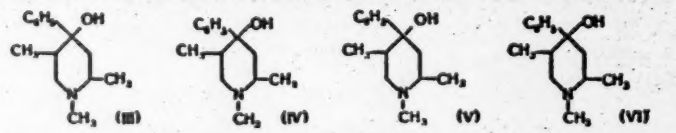
(Presented by Academician B. A. Kazanskii, March 4, 1959)

It has recently been shown [1] that 1, 2, 5-trimethyl-4-piperidone prepared by condensation of propenyl isopropenyl ketone with methylamine is a mixture of the cis and trans isomers (I) and (II), of which the more stable trans isomer (II), which is the predominant form obtained under alkaline isomerization conditions, was obtained in the individual state. This permitted synthesis of all four geometric isomers of 1, 2, 5-trimethyl-4-phenyl--4-piperidol (III), (IV), (V), and (VI), the propionates of which exhibited varying degrees of anesthetic activity [2]. It was established that the sedative action of (III), (IV), (V), and (VI) exceeds that of morphine by factors of, respectively, 2, 8, 4, and 4-6.



(I) (II)



(III) (IV) (V) (VI)

Promedol alcohol, m.p. 107-108°

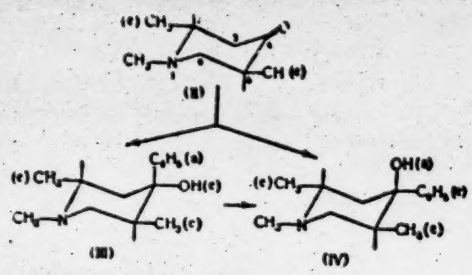
α-Promedol alcohol, m.p. 106-107°

Isopromedol alcohol, m.p. 102-103°

δ-Promedol alcohol, m.p. 109-110°

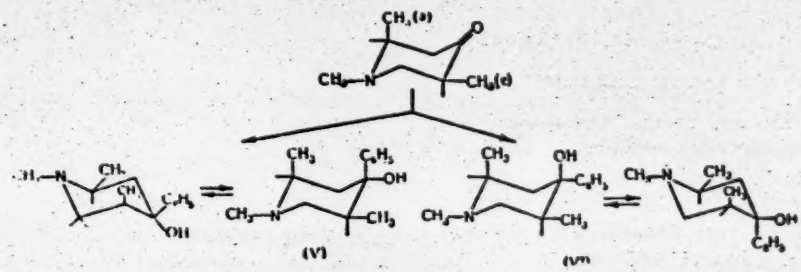
With the aim of clarifying the connection between th physiological activity and the steric structure of this class of compounds, we undertook a study of the stereochemistry of the isomeric phenyl alcohols, which permitted us to ascribe to them the configurations shown above. As was previously established [1], during the reaction of trans-piperidone with phenyllithium, a mixture (4:1) of the isomeric phenyl alcohols (III) and (IV) is formed, and these should differ only in the configuration at C_4. It was found that isomer (IV) is more readily dehydrated and more difficultly esterified than (III), and, consequently, it must contain an axial hydroxyl group at C_4, as shown in the scheme on the following page.

Consideration of molecular models show that alcohol (IV) with a phenyl group in the equatorial position is thermodynamically more favored, and it was indeed found that the isomeric alcohol (III) could be readily converted into (IV) in reactions proceeding with Walden inversion at C_4 [1]. All of these data quite persuasively show that promedol alcohol (III), in which there is trans disposition of the methyl groups, has cis disposition of the phenyl

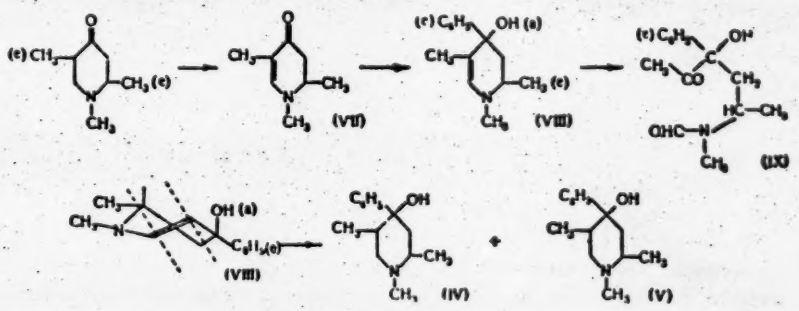


group at C_4 and the methyl group at C_5, while α-promedol alcohol (IV) is the isomer with trans disposition of these groups. Previously, and without sufficient basis, the contrary configurations at C_4 were erroneously ascribed to these alcohols [3].

It is considerably more difficult to establish proof of the configurations of isomers (V) and (VI), in which the cis distribution of the methyl groups can promote ready conversion of the rings. Owing to the presence of such transformations, cis isomers (V) and (VI) are not appreciably distinct in trans-esterification and trans-elimination reactions.



The question of the conformations of these isomers can be quite unequivocally decided by a study of the products of the catalytic hydrogenation of the previously obtained [1] 1, 2, 5-trimethyl-4-phenyl-Δ^5-dehydro-4-piperidol (VIII), the structure and configuration of which were shown by special experiments. This unsaturated Δ^5--4-phenylpiperidol (VIII), which is obtainable in good yield by the interaction of 1, 2, 5-trimethyl-Δ^5-dehydro-4--piperidone (VII) with phenyllithium, proved to be very easily dehydrated (even under conditions under which the propionate is prepared), which is proof of the presence of an axial hydroxyl group at C_4. Since the starting material in this synthesis scheme is trans-piperidone (II) which has the more stable diequatorial disposition of the methyl groups, the product Δ^5-4-phenylpiperidol (VIII) must have the same more favored equatorial disposition of the methyl group at C_2, and, consequently, will have a cis configuration of this substituent with respect to the phenyl groups at C_4. The structure of the Δ^5-4-phenylpiperidol (VIII) was shown by oxidation to compound (IX), the structure of which was confirmed by infrared spectroscopy. It was found that product (IX) has characteristic absorption bands corresponding to the presence of the C = O bond of a tertiary amide (1642 cm^{-1}), an unconjugated keto group (1706 cm^{-1}), and an associated hydroxyl (3270 cm^{-1}), the formation of which is possible only by oxidation of a double bond at C_5 of the piperidine ring.



As seen from the steric formula of Δ^5-4-phenylpiperidol (VIII), catalytic hydrogenation (cis addition of hydrogen) of this compound must proceed without steric selectivity. In the case of the addition of hydrogen from the side opposite to the hydroxyl group, 1, 2, 5-trimethyl-4-phenyl-4-piperidol with trans disposition of the methyl groups and with cis disposition of the methyl group at C_5 and the hydroxyl at C_4 (isomer IV) must be formed. In the case of cis addition of hydrogen from the other side, the resulting product will have cis disposition of the methyl groups and trans disposition of the methyl group at C_5 and the hydroxyl at C_4 (isomer V).

It was found that catalytic hydrogenation of 1, 2, 5-trimethyl-4-phenyl-Δ^5-dehydro-4-piperidol actually yields a mixture of isomers, from which were isolated in a ratio of approximately 5:1 isomer (IV) and a new isomer with an m.p. of 102-103°, which proved to be identical to isopromedol alcohol (V). These data, which are additional confirmation of the configuration of α-promedol alcohol (IV), show that the third isomer (isopromedol alcohol V), which is prepared from cis-piperidone (I), has cis disposition of the methyl groups and, similarly to promedol alcohol (III), cis disposition of the phenyl group at C_4 and of the methyl group at C_5. In conformity with this, the fourth isomer (δ-promedol alcohol VI) will have the only configuration possible for it cis disposition of the methyl groups and trans disposition of the phenyl group at C_4 and of the methyl groups at C_5.

EXPERIMENTAL

Isolation of δ-promedol alcohol (VI). The mother liquors remaining from the isolation of isopromedol, promedol, and α-promedol alcohol (IV), which were prepared from 1 kg of a mixture of piperidones (I) and (II) rich in (I) [1], were combined, treated with a base to saponify the esters and to decompose the salts, and distilled under vacuum. The fraction boiling at 135-150° at 2 mm (about 30 g) was treated with 30 ml of a saturated alcoholic solution of HCl, and 23 g of the hydrochloride of the δ-isomer of 1, 2, 5-trimethyl-4-phenyl-4-piperidol was obtained; m.p. 264-265° (from alcohol).

Found %: N 5.55; 5.70 $C_{14}H_{20}ONCl$. Calculated %: N 5.49

The base of δ-isomer (VI) melted 109-110°.

Found %: C 76.53; 76.70; H 9.37; 9.55; N 6.16; 6.21 $C_{14}H_{19}ON$. Calculated %: C 76.70; H 9.60; N 6.40

2.4 g of the hydrochloride of the δ-isomer of the propionate of 1, 2, 5-trimethyl-4-phenyl-4-piperidol, m.p. 196-197° (from a mixture of alcohol and ether), was obtained by treatment of 2 g of (VI) with a mixture of 2 ml of dichloroethane and 2 ml of propionyl chloride and allowing the mixture to stand for 12 hours at 20°.

Found %: C 64.99; 65.05; H 8.08; 7.98; N 4.46; 4.50 $C_{17}H_{26}NO_2Cl$. Calculated %: C 65.47; H 8.40; N 4.49

Dehydration of 1, 2, 5-trimethyl-4-phenyl-4-piperidols (III), (IV), (V), and (VI). a) 3 g of promedol alcohol (III) was dissolved in 10 ml of 1:1 HCl, and the solution was heated for 2 hours on a boiling water bath; the solution was then cooled and treated with 10 ml of concentrated NH_4OH. The oil which separated completely crystallized after standing for 10 minutes; recrystallization of this material from hexane gave 2 g of the original alcohol (III) with an m.p. of 106-107°.

b) Similarly, heating 3 g of α-promedol alcohol (IV) in 10 ml of HCl and treating with ammonia gave an oil, which was extracted with ether and distilled under vacuum. 1.5 g of dehydration product, b.p. 85° at 2.5 mm [4], and 0.4 g of the original alcohol (IV), b.p. 145-146°/4 mm, m.p. 107-108°, were obtained.

c) Dehydration of 3 g of isopromedol alcohol (V) or 3 g of δ-promedol alcohol (VI) under the same conditions gave 2.5 g of the identical dehydration product with a b.p. of 108-110°/4 mm; m.p. of the hydrochloride 191-192°.

Found %: C 70.77; 70.90; H 8.49; 8.53; N 6.01; 6.19 $C_{14}H_{18}NCl$. Calculated %: C 70.90; H 8.43; N 5.90

A mixture of the hydrochloride of the product from the dehydration of alcohol (V) with the hydrochloride of the product of the dehydration of alcohol (IV) (m.p. 185-186°) melted at 150-160°.

Oxidation of 1, 2, 5-trimethyl-4-phenyl-Δ^5-dehydro-4-piperidol (VIII). 10 g of Δ^5-4-phenyldehydropiperidol (VIII) was dissolved in 100 ml of acetone, and a solution of 17.5 g of $KMnO_4$ in 500 ml of acetone was then slowly added with stirring. The precipitated manganese dioxide was filtered, the filtrate was evaporated under vacuum, the residue was extracted with ether, the ether was distilled, and the liquid residue was treated with 10 ml of 85% hydrazine hydrate. The reaction mixture was allowed to stand overnight; it was then evaporated under vacuum at 100°, and 10 ml of benzene was added to the residue. 4 g of the hydrazone of 2-methylformyl--amino-4-phenyl-4-hexanol-5-one (IX) precipitated; m.p. 138-140° (from benzene).

Found %: C 63.16; 63.29; H 8.00 7.90; N 15.82; 15.73 $C_{14}H_{22}O_2N_2$. Calculated %: C 63.50; H 8.32; N 15.90

Treatment of the hydrazone with HCl (1:1) and alkalization gave ketone (IX), m.p. 97-98° (from ether).

Found %: C 66.95; 66.81; H 7.62; 7.69 $C_{24}H_{29}O_2N$. Calculated %: C 67.4; H 7.63

The infrared spectrum and characteristic absorption bands at 1642 mμ (tertiary amide), 1706 mμ (ketone), and 3270 mμ (associated hydroxyl).

Dehydration of 1, 2, 5-trimethyl-4-phenyl-Δ^5-dehydro-4-piperidol (VIII). A solution of 5 g of (VIII) in 10 ml of dichloroethane was cooled with ice, 5 ml of propionyl chloride was added, and the resulting solution was allowed to stand for 7 days at room temperature; the dichloroethane and propionyl chloride were then distilled under vacuum (the bath temperature did not exceed 50°), and the residue was dissolved in alcohol and treated with ether.

From the resulting precipitate was isolated 0.5 g of the hydrochloride of 1, 2, 5-trimethyl-4-phenyldihydropyridine with an m.p. of 255-256° (from a mixture of alcohol and ether).

Found %: C 69.81; H 7.33; N 6.06 $C_{14}H_{20}NCl\cdot\frac{1}{4}H_2O$. Calculated %: C 70.06; H 7.50; N 5.83

Hydrogenation of 1, 2, 5-trimethyl-4-phenyl-Δ^5-dehydro-4-piperidol. A solution of 11 g of dehydropiperidol (VIII) in 50 ml of methanol was hydrogenated over Pt catalyst; 1200 ml of H_2 was absorbed in 8 hours. The solution was filtered free of catalyst and evaporated under vacuum, and the resulting crystalline precipitate was recrystallized from isooctane. 4.5 g of α-promedol alcohol (IV) was separated, and the mother liquor was then distilled under vacuum. The fraction boiling at 125-140°/2 mm was treated with 5 ml of a saturated alcoholic solution of HCl, and 1.45 g of the hydrochloride of α-promedol alcohol crystallized; treatment of the mother liquor with ammonia gave 1.2 g of isopromedol alcohol (V), m.p. 102-103°, a mixture of which with a sample of the previously obtained material showed no depression of the melting point.

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SYNTHESIS OF TRIETHYLSILOXY DERIVATIVES OF VANADIUM AND ANTIMONY

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The development of investigations on the synthesis of polymers, containing alternate atoms of metal and oxygen in the basic chain, is directly connected with the development of methods of synthesizing monomeric compounds with an Si—O—Me bond and among these, trialkylsiloxy derivatives of metals with the general formula $(R_3SiO)_nMe$, where n is the valence of the metal, are of definite interest.

Among the methods described in the literature at the present time, an interesting route to the synthesis of compounds of this type is the reaction of trialkylsilanolates of sodium and some other metals with metal halides by the scheme

$$MeCl_n + n\,R_3SiONa \rightarrow Me(OSiR_3)_n + n\,NaCl.$$

Using this route, we synthesized for the first time tetrakis-(trimethylsiloxy)-titanium [1], and also tetrakis-(triethylsiloxy)-titanium [2], tetrakis-(dimethylphenylsiloxy)-titanium [3] and tetrakis-(triethylsiloxy)-tin [2].

In the present work we extended the method described above to the synthesis of vanadium and antimony triethylsilanolates by the following reaction schemes:

$$3(C_2H_5)_3SiONa + VOCl_3 \rightarrow OV[OSi(C_2H_5)_3]_3 + 3NaCl,$$
$$3(C_2H_5)_3SiONa + SbCl_3 \rightarrow Sb[OSi(C_2H_5)_3]_3 + 3NaCl.$$

The experiments performed showed that these reactions gave product yields of 60—70% of theoretical.

On investigating the properties of lead triethylsilanolate, which we synthesized previously [4], we established that this compound had a considerable reactivity. Thus, treatment of a complex of lead triethylsilanolate with titanium tetrachloride or vanadium oxychloride formed tetrakis-(triethylsiloxy)-titanium of tris-(triethylsiloxy)-vanadate, respectively, by the schemes

$$2\{2Pb[OSi(C_2H_5)_3]_2 \cdot Pb(OH)_2\} + 3TiCl_4 \rightarrow 2Ti[OSi(C_2H_5)_3]_4 + 6PbCl_2 + Ti(OH)_4,$$
$$3\{2Pb[OSi(C_2H_5)_3]_2 \cdot Pb(OH)_2\} + 4VOCl_3 \rightarrow$$
$$\rightarrow 4VO[OSi(C_2H_5)_3]_3 + 6PbCl_2 + 3Pb(OH)_2.$$

These reactions, which we applied to titanium tetrachloride and vanadium oxychloride, are of general value for preparing trialkylsilyl derivatives of various elements.

Investigations of the infrared spectra of some of the compounds synthesized, carried out in the V. I. Lenin All-Union Electrotechnical Institute by N. Gashnikova, showed that the characteristic vibration frequencies (in cm^{-1}) for the compounds investigated had the following values: $VO[OSi(C_2H_5)_3]_3$, 2967, 2950, 2882, 1592, (V=O), 2468, 1458, 1232, 1209, 1060 (broad), 1004, 989, 979, 962, 909, (V—O—?), 875 (V—O—?), 727. $2Pb[OSi(C_2H_5)_3]_2 \cdot Pb(OH)_2$, 2967, 2907, 2950, 2882, 1481, 1460, 1239, 1210, 1053, 1000, 988, 962, 861, (Pb—O), 724.

The properties of the compounds synthesized are presented in Table 1.

TABLE 1

	Name of substance	Formula of substance	B.p., °C/mm	n_D^{20}	d_4^{20}	Found %					Calculated %					Yield %
						C	H	Si	Me		C	H	Si	Me		
1	Tris-(triethylsiloxy)-vanadate	$O=V[OSi(C_2H_5)_3]_3$	180,5/3,5	1,4820	0,9816	46,88 46,86	10,22 10,38	17,58 17,41	10,68 10,54		46,92	9,84	18,27	11,06		60
2	Tris-(triethylsiloxy)-stibine	$Sb[OSi(C_2H_5)_3]_3$	100—102/1,5	1,4681	1,1037	41,60 41,48	9,28 9,35	16,08 16,11	23,20 23,30		41,93	8,79	16,33	23,62		56

EXPERIMENTAL

Tris-(triethylsiloxy)-vanadate. Into a three-necked flask, fitted with a stirrer, condenser with a calcium chloride tube and a dropping funnel, was placed a solution of 37.5 g (0.24 mole) of sodium triethylsilanolate in 200 ml of dry benzene. With careful stirring, a solution of 14 g (0.08 mole) of vanadium oxychloride in 50 ml of dry benzene was added to the solution dropwise over a period of 40 min. At the end of the reaction, the solution was filtered free of precipitate, the precipitate washed on the filter with 100 ml of dry benzene, the benzene distilled from the filtrate on a water bath and the residue then vacuum distilled. We obtained 21 g (60% of theoretical) of a light-yellow liquid with b.p. 186.5°/3.5 mm; d_4^{20} 0.9816; n_D^{20} 1.4820.

Found %: C 46.88; 46.86; H 10.22; 10.38; Si 17.58; 17.41; V 10.68; 10.54 $C_{18}H_{45}O_4Si_3V$. Calculated %: C 46.92; H 9.84; Si 18.27; V 11.06

Tris-(triethylsiloxy)-stibine. This product was obtained from 46 g (0.3 mole) of sodium triethylsilanolate and 23 g (0.1 mole) of antimony trichloride in 400 ml of benzene by an analogous method.

Fractionation yielded 22 g (56% of theoretical) of a clear, colorless liquid with b.p. 160—162°/1.5 mm; d_4^{20} 1.1037; n_D^{20} 1.4681.

Found %: C 41.60; 41.48; H 9.28; 9.35; Si 16.08; 16.11; Sb 23.26; 23.30 $C_{18}H_{45}O_3Si_3Sb$. Calculated %: C 41.93; H 8.79; Si 16.33; Sb 23.62.

Tetrakis-(triethylsiloxy)-titanium. The reaction was carried out in the same apparatus. Into the flask was placed a solution of 58 g (0.05 mole) of the derivative of bis-triethylsiloxylead in 100 ml of dry benzene. A solution of 14.4 g (0.074 mole) of titanium tetrachloride in 50 ml of benzene was added to the solution dropwise over a period of 1.5 hours. The precipitate was removed, the benzene distilled from the filtrate and the residue vacuum distilled. We obtained 14 g (50% of theoretical) of tetrakis-(triethylsiloxy)-titanium with b.p. 176—178°/2.5 mm and m.p. 96°.

Tris-(triethylsiloxy)-vanadate. This substance was obtained analogously to tetrakis-(triethylsiloxy)-titanium from 67.4 g (0.06 mole) of lead derivative and 12 g (0.02 mole) of vanadium oxychloride in 200 ml of benzene. Distillation of the filtrate after removal of the lead chloride precipitate yielded tris-(triethylsiloxy)-vanadate with b.p. 169—171°/1.5 mm; d_4^{20} 0.9809; n_D^{20} 1.4812.

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CATALYTIC HYDROGENATION OF DIENE HYDROCARBONS WITH AN ISOLATED SYSTEM OF DOUBLE BONDS IN THE PRESENCE OF PLATINUM AND PALLADIUM

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Metallic platinum and palladium which have a general capacity for catalyzing the addition of hydrogen to unsaturated compounds behave differently during hydrogenation.

Thus, for example, in the incomplete hydrogenation of monoolefins in the liquid phase in the presence of palladium, the reaction products contain new monoolefins formed by transposition of the double bonds in the original hydrocarbon [1, 2]. Such a transposition of bonds does not occur in the presence of platinum [2, 3].

It seemed interesting to us to determine how dienes with an isolated system of double bonds would behave under these conditions. It is known that in heterogeneous catalysis at temperatures above 200° such dienes are isomerized in the presence of palladium and platinum into dienes with a conjugated system of double bonds [4]. In this work we used hexadiene-1, 5 (diallyl), 2-methylhexadiene-2, 5, 2-methylhexadiene-1, 5 and 2, 5-dimethylhexadiene-1, 5 (dimethallyl). To them was added half a molecule of hydrogen at room temperature in the presence of platinum and palladium; in each case there should have been formed a mixture of equal amounts of mono- and diolefin.

It was found that with partial hydrogenation of hexadiene-1, 5 in the presence of platinum, the reaction products contained not only hexene-1, but also n-hexane together with unreacted diallyl:

$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 \xrightarrow[Pt]{+0.5\,H_2} \begin{cases} \rightarrow CH_2{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_3 & (27\%) \\ \rightarrow CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3 & (12\%) \\ \rightarrow CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 & (61\%) \end{cases}$$

In the presence of palladium the hydrogenation product consisted of hexene-1 and its isomer, hexene-2; together with unreacted hexadiene-1, 5, its isomerization product, hexadiene-1, 4 appeared. n-Hexane was absent:

$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 \xrightarrow[Pd]{+0.5\,H_2} \begin{cases} \rightarrow CH_2{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_3 & (23\%) \\ \rightarrow CH_3{-}CH{=}CH{-}CH_2{-}CH_2{-}CH_3 & (27\%) \\ \rightarrow CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 & (33\%) \\ \rightarrow CH_2{=}CH{-}CH_2{-}CH{=}CH{-}CH_3 & (17\%) \end{cases}$$

It should be emphasized that the hydrogenation products of diallyl with palladium did not contain the expected diene with a conjugated system of double bonds. The hydrogenation products of 2-methylhexadiene-1, 5 and 2, 5-dimethylhexadiene-1, 5 did not contain conjugated dienes, i.e. in these cases also only one of the two double bonds underwent transposition.

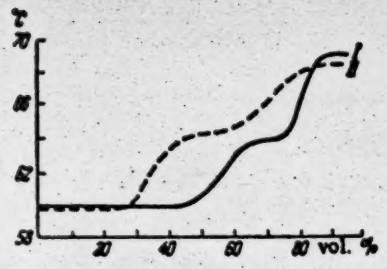

Fig. 1. Distillation curves of hydrogenation products of hexadiene-1, 5: I — in the presence of platinum, II — in the presence of palladium.

TABLE 1

Fract. No.	B.p., °C at 760 mm	Amt. in g	n_D^{20}	d_4^{20}	Unsaturation in %
1	59.2—59.5	11.7	1.4042	0.6910	200
2	59.6—62.7	4.1	1.3990	0.6850	172
3	62.8—63.7	4.4	1.3890	0.6739	105
4	63.8—68.2	1.7	1.3859	0.6684	64
Res.	—	2.6	1.3770	0.6610	9

In contrast to 1, 5-dienes, under the same conditions 2-methylhexadiene-2, 5 was isomerized into a diene with a conjugated system of double bonds, namely 2-methylhexadiene-2, 4, to approximately 15%.

Apparently the absence of conjugated dienes in the hydrogenation of 1, 5-dienes with palladium should be explained by an unfavorable ratio of the rates of hydrogenation and isomerization, proceeding on the palladium surface. It should also be noted that both reactions affected only one of the two double bonds of the diene. Transposition of the double bonds during hydrogenation of unsaturated compounds with palladium may influence the kinetics of hydrogen addition. Therefore, conclusions on the relation between the structure of the compound hydrogenated and the rate of hydrogen addition should be drawn with care and considering these possible complications.

TABLE 2

Hydrocarbon	B.p.	n_D^{20}	d_4^{20}	Lit. cit.	Hydrocarbon	B.p.	n_D^{20}	d_4^{20}	Lit. cit.
Hexadiene-1, 4	65	1.415	0.699	(5)	2-Methylhexene-2	95.4	1.4106	0.7082	(5)
Hexadiene-1, 3	73	1.438	0.705	(5)	2-Methylhexene-4 cis	91.0	1.400	0.700	(5)
Hexadiene-2, 4	80	1.450	0.720	(5)	2-Methylhexene-4 trans	86.0			
Hexene-1	63.5	1.3879	0.6732	(5)	2-Methylhexene-5	85.3	1.3966	0.6920	(5)
Hexene-2 cis	68.8	1.3977	0.6869	(5)	2, 5-Dimethylhexadiene-1, 4	116.5	1.437	0.749	(6)
Hexene-2 trans	67.9	1.3935	0.6784	(5)	2, 5-Dimethylhexadiene-2, 4	134.5	1.4781	0.7615	(6)
Hexene	68.7	1.3749	0.6594	(5)	2, 5-Dimethylhexene-1	111.6	1.4105	0.7172	(5)
2-Methylhexadiene-2, 5	91.5–92.0	1.4390	0.7258	(6)	2, 5-Dimethylhexene-2	112.2	1.4140	0.7203	(5)
2-Methylhexadiene-2, 4	111.5	1.4680	0.7449	(5)					
2-Methylhexene-1	92.0	1.4094	0.7030	(6)					

TABLE 3

Fract. No.	B.p., °C at 760 mm	Amt., g	n_D^{20}	d_4^{20}	Unsaturation, %
1	59.6—60.0	15.2	1.4042	0.6909	200
2	60.1—63.1	4.1	1.3975	0.6838	159
3	63.2—63.8	6.8	1.3910	0.6763	114
4	63.9—64.8	6.1	1.3970	0.6832	128
5	64.9—66.0	4.1	1.4045	0.6909	173
6	66.1—67.0	2.4	1.4000	0.6848	129
7	67.1—68.3	10.6	1.3948	0.6794	97
Res.	—	1.9	1.3998	0.6875	97

TABLE 4

Fract. No.	B.p., °C at 760 mm	Amt. g	n_D^{20}	d_4^{20}	Unsaturation, %
1	86.0—86.7	2.1	1.4030	0.6970	121
2	86.7—88.1	4.2	1.4089	0.7055	147
3	88.1—88.5	2.8	1.4125	0.7118	170
4	88.5—90.7	4.3	1.4140	0.7131	168
5	90.8—91.5	10.7	1.4130	0.7114	152
6	91.5—91.9	9.9	1.4111	0.7110	138
7	92.0—93.7	2.9	1.4161	0.7165	149
Res.	—	3.6	1.4138	0.7110	103

EXPERIMENTAL

Characteristics of dienes used. Hexadiene-1, 5: b.p. 59.7°, n_D^{20} 1.4042, d_4^{20} 0.6909. 2-methylhexadiene-1, 5: b.p. 88.2°, n_D^{20} 1.4184, d_4^{20} 0.7196. 2-methylhexadiene-2, 5: b.p. 93.0°, n_D^{20} 1.4258, d_4^{20} 0.7252. 2, 5-dimethylhexadiene-1, 5: b.p. 114.2°, n_D^{20} 1.4293, d_4^{20} 0.7412.

Experimental procedure. The hydrogenation was carried out at room temperature and atmospheric pressure in a medium of 95% ethyl alcohol [2]. The amounts of platinum and palladium blacks taken represented 2.3 mole percent with respect to diene. The composition of the reaction products was established by distillation on a column of 80 t.p.

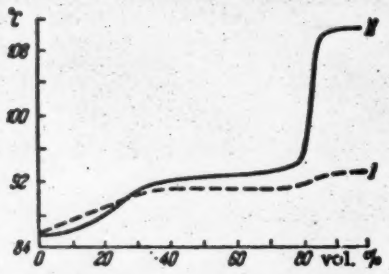

Fig. 2. Distillation curves of hydrogenation products: I – 2-methylhexadiene-1, 5, II – 2-methylhexadiene-2, 5.

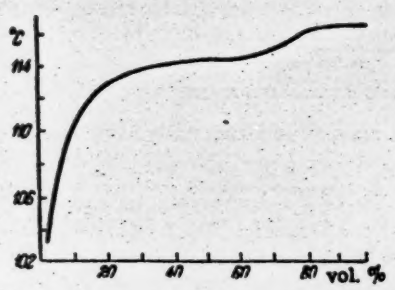

Fig. 3. Distillation curve of 2, 5-dimethylhexadiene-1, 5 hydrogenation products.

TABLE 5

Fract. No.	B.p., °C at 760 mm	Amt., g	n_D^{20}	d_4^{20}	Unsaturation, %
1	85,8—86,2	1,1	1,3990	0,6927	102
2	86,3—88,1	1,5	1,4012	0,6951	108
3	88,2—91,0	1,5	1,4035	0,7038	131
4	91,1—93,0	5,7	1,4188	0,7174	178
5	93,7—105	1,4	1,4167	0,7174	—
6	105—111	1,9	1,4338	0,7465	—

TABLE 6

Fract. No.	B.p., °C at 760 mm	Amt., g	n_D^{20}	d_4^{20}	Unsaturation, %
1	103,0—112,1	3,6	1,4079	0,7101	100
2	112,2—113,9	4,6	1,4145	0,7193	108
3	113,9—114,4	6,5	1,4185	0,7237	124
4	114,4—115,0	3,6	1,4230	0,7305	153
5	115,0—116,5	4,4	1,4311	0,7404	188
6	116,5	2,4	1,4360	0,7444	189

Hydrogenation of diallyl in the presence of platinum black. 27.6 g of diene was taken for hydrogenation; we obtained 26.5 g of hydrogenation products. The distillation curve is presented in Fig. 1 and the characteristics of the fractions in Table 1.

A comparison of the properties of the fractions obtained with the properties of the hydrocarbons, which could have been formed by hydrogenation and isomerization of diallyl (Table 2), shows that fraction 1 was original diallyl, fraction 3, hexene-1 and the residue, hexane.

Hydrogenation of diallyl in the presence of palladium black. 55.2 g of diene was taken for reaction; we obtained 52.7 g of hydrogenation products. The distillation curve is given in Fig. 1 and the characteristics of the fractions in Table 3.

Fraction 1 was diallyl, fraction 3 was similar to hexene-1 and, judging by unsaturation, fraction 5 contained a considerable amount of diene. Further distillation of this fraction on a column yielded a narrow fraction with b.p. 65.3 – 65.4°, n_D^{20} 1.4081, d_4^{20} 0.6974.

In all characteristics, this fraction was close to hexadiene-1, 4.

Hydrogenation of 2-methylhexadiene-1, 5 in the presence of palladium black. 43.2 g of diene was taken for hydrogenation; we obtained 41.9 g of hydrogenation products. The distillation curve is given in Fig. 2 and the characteristics of the fractions in Table 4.

Comparison of the properties of the fractions obtained with those of the possible reaction products (Table 2) shows that the reaction mixture was very complex and it was only possible to say with certainty that the mixture did not contain the diene with a conjugated system of double bonds, 2-methylhexadiene-2, 4.

Hydrogenation of 2-methylhexadiene-2, 5 in the presence of palladium black. 14.2 g of diene was taken for hydrogenation; 13.5 g of hydrocarbons was obtained after hydrogenation. The distillation curve is given in Fig. 2 and the characteristics of the fractions in Table 5.

Fraction 6 contained the diene with a conjugated system of double bonds, 2-methylhexadiene-2, 4 (Table 2), and this represented about 15% of the reaction products.

Hydrogenation of 2, 5-dimethylhexadiene-1, 5 in the presence of palladium black. 27.4 g of diene was taken for hydrogenation; we obtained 26.5 g of hydrogenation products. The distillation curve is presented in Fig. 3 and the characteristics of the fractions in Table 6.

Fractions 5 and 6 apparently contained 2, 5-dimethylhexadiene-1, 4 (Table 2).

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ANALYSIS OF A MIXTURE OF DIMETHYL ESTERS OF BENZENEDICARBOXYLIC ACIDS BY MEANS OF GAS-LIQUID CHROMATOGRAPHY

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(Presented by Academician B. A. Kazanskii April 1, 1959)

Benzenedicarboxylic acids (phthalic, isophthalic and terephthalic) have recently acquired great importance as intermediates in the preparation of certain plastics; this applies particularly to terephthalic acid, which is used for the production of artificial fibers of the polyester type. A determining factor for the quality of the fibers is the high purity of the terephthalic acid or its dimethyl ester, the starting material for the production of poly-(ethylene terephthalate).

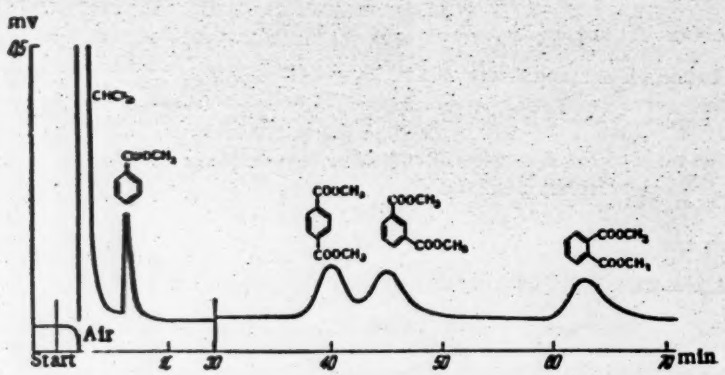

Fig. 1. Chromatogram of a mixture of methyl benzoate and dimethyl benzenedicarboxylates on a column (4.80 m long) with erythritol as the stationary phase at 165° C.

The methods described in the literature [1 – 6] for determining the purity of terephthalic acid and its isomers and their derivatives are, on the one hand, very laborious and not very accurate and on the other, do not allow the simultaneous determination of all three isomers. A mixture of terephthalic and isophthalic acids was separated by a gravimetric method, based on the different solubilities of their thallium salts [1]. By means of chromatography on silica gel [2, 3] and on paper [4], phthalic acid has been separated from a mixture of isophthalic and terephthalic acids, but this mixture remained unresolved. Micheel and Schweppe [5] converted a mixture of isomeric benzenedicarboxylic acids into hydroxamic acids, which were then chromatographed on paper. However, the R_f values obtained for isophthalic and terephthalic acids were very close to each other so that the method was only applicable to a limited extent. Since isophthalic and terephthalic acids could not be

TABLE 1

Chromatographic Spectrum of a Mixture of Methyl Benzoate and Dimethyl Benzenedicarboxylates

Substance	B.p., °C	Relative elution volume
Methyl benzoate	198	0,10
Dimethyl phthalate	264	1,42
Dimethyl isophthalate*	269	1,00
Dimethyl isophthalate	274	0,88

* V_g^0 of dimethyl isophthalate = 85

separated by paper chromatography, Franc [6] described the nitration of a mixture of them with subsequent separation of the nitro derivatives obtained on paper. Phthalic acid (its 3- and 4--nitro derivatives) interfered in this case.

We established that by the use of gas — liquid chromatography [7] on certain stationary phases containing hydroxy groups, it was possible to achieve the desired separation on the basis of the different associations of the separate isomeric methyl esters with the stationary phase. The presence of the benzoic ester had no effect on the results of the chromatographic analysis since its elution characteristic was of a different order from those of the dicarboxylic esters mentioned above.

For the work we used a Griffin and George (London) apparatus of the normal plan with a platinum flow detector based on thermal conductivity, and a recording millivoltmeter (0 — 1 mv). Nitrogen was the carrier gas used. The operating temperature was 165° and the column packing used was the porous material "Porovina" [8] with a grain size of 0.20 — 0.30 mm, impregnated with 10.8% of erythritol. The characteristic elution data were determined with a column with a packing containing 18.65 g of active material; the data were expressed relative to dimethyl isophthalate. The specific elution volume V_g^0 for dimethyl isophthalate was calculated. The results are presented in Table 1. The course of a chromatographic analysis is presented in Fig. 1.

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CERTAIN FEATURES OF NONEQUILIBRIUM POLYCONDENSATION *

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As one of us showed previously in a series of investigations [1], equilibrium polycondensation proceeding by the interaction of a diamine with dicarboxylic acids or of the latter with glycols has a series of special characteristics.

One of the most important characteristics of equilibrium polycondensation is the reversible character of both the main polymer synthesis reaction:

$$x\,HOOC(CH_2)_4COOH + x\,H_2N(CH_2)_6NH_2 \rightleftarrows$$
$$\rightleftarrows HO[-CO(CH_2)_4CONH(CH_2)_6NH-]_xH + (2x-1)H_2O,$$

and those associated conversions, exchange reactions, which proceed simultaneously [2]. These reactions proceed between growing polyamide molecules through the terminal groups and the amide bonds in the macromolecule [3]. Such exchange reactions, which are for the most part of a destructive character, cause a definite and quite narrow molecular weight distribution of the polymer formed [4].

The presence of exchange reactions leads to an equilibrium in polycondensation being established in the system and this is designated as a "polycondensation equilibrium" [5]. As a result of this equilibrium, an excess of one of the starting components has a great effect on the molecular weight of the product obtained [6] as is shown in Fig. 2. Additions of monofunctional substances act in exactly the same way and lower the molecular weight of the polymer obtained.

We undertook this investigation to determine how these relations varied when the polycondensation was carried out as a nonequilibrium process. The interaction of diacid chloride of dicarboxylic acids with diamines can serve as an example of this type of reaction

$$x\,ClCO(CH_2)_4COCl + x\,NH_2(CH_2)_6NH_2 \rightarrow [-CO(CH_2)_4CONH(CH_2)_6NH-]_x + 2x\,HCl.$$

If this reaction occurs at the boundary of two phases with the starting reagents used as solutions in two immiscible liquids [7], then it proceeds very rapidly and at low temperatures, i.e. under conditions when there are no exchange reactions.

We investigated the reaction between hexamethylenediamine and adipyl chloride. For the reaction we used an aqueous solution of hexamethylenediamine, to which the necessary amount of alkali had been added, and a benzene solution of adipyl chloride.

The effect of the concentration of the starting materials on the yield and the molecular weight of the polymers formed was first determined. As Fig. 1 shows, the optimal concentration giving the highest yield of products

* Only part of the results obtained is presented in the article. A fuller description of the work will be given in a detailed article in another place.

** P. A. Allevskii participated in the experimental work.

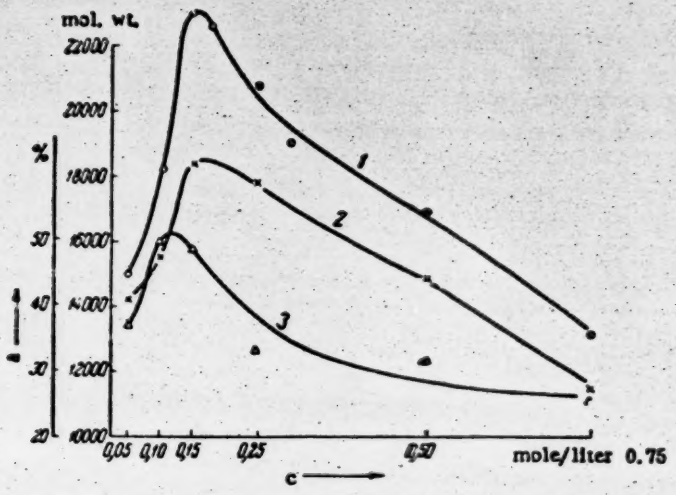

Fig. 1. Change in molecular weight (1, 2) and yield (3) of polyamide in relation to the starting concentrations of the reagents: 1) with removal of the polyamide from solution; 2) with stirring of the starting solutions; 3) change in yield of polyamide with stirring

TABLE 1

Amt. of excess component, mole %	With excess hexamethylenediamine			With excess adipyl chloride		
	spec. viscosity of 0.5% solution in tricresol at 20° C	mol. wt.	yield, % of theoretical	spec. viscosity of 0.5% solution in tricresol at 20° C	mol. wt.	yield, % of theoretical
0	0,53	14300	32	0,53	14300	32
5	0,55	14700	30	0,58	15400	39
10	0,53	14300	25	0,54	14500	22
25	0,49	13400	16	0,53	14300	33
50	0,55	14800	35	0,49	13400	33
100	0,52	14100	28	0,57	15400	22

Footnote: The reaction was carried out by stirring 0.15 M solutions of the starting reagents for 10 min. at a stirrer speed of about 1000 rpm.

with the highest molecular weight was found to be 0.15 mole/liter of solution. Therefore all subsequent experiments were carried out at this concentration with the two starting reagents used as solutions of identical concentration.

To determine the effect of the ratio of starting materials on the molecular weight of the polymers formed, we carried out a series of experiments in which either one or the other of the starting materials was taken in excess. In both cases up to 100 mole% excess of the starting materials was used.

However, despite the presence of such great excesses of this or that starting reagent, the polyamides obtained had practically the same molecular weights. The variation in the values of the molecular weights lay within the limits of experimental error as can be seen from Table 1.

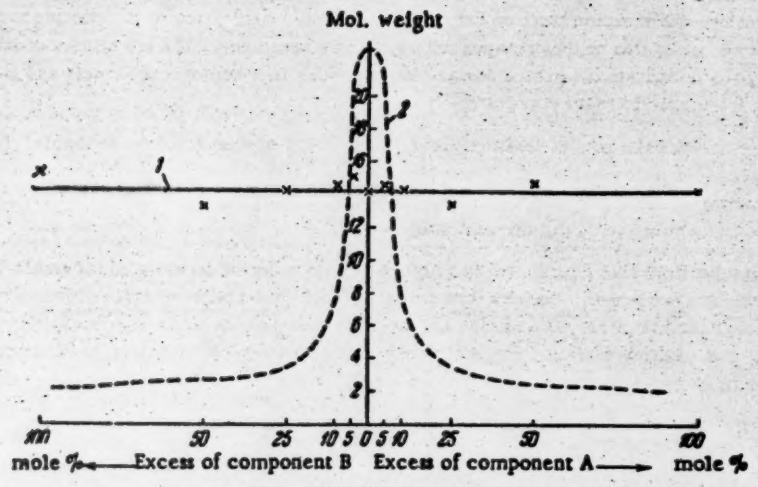

Fig. 2. Dependence of polyamide molecular weight on excess of starting components: 1) in nonequilibrium polycondensation in relation to excess of hexamethylenediamine (A) and adipyl chloride (B); 2) in equilibrium polycondensation in relation to excess of hexamethylenediamine (A) and adipic acid (B)

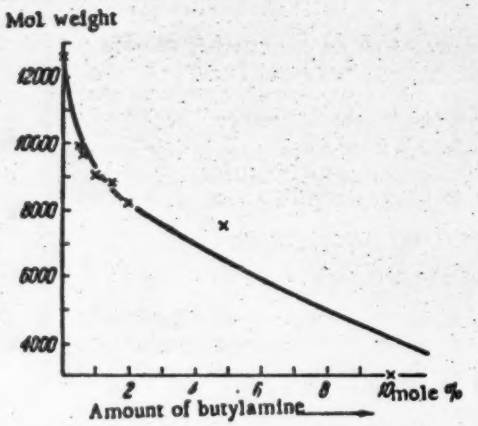

Fig. 3. Change in molecular weight of polyamide in relation to the addition of various amounts of butylamine (the polymer was obtained with stirring)

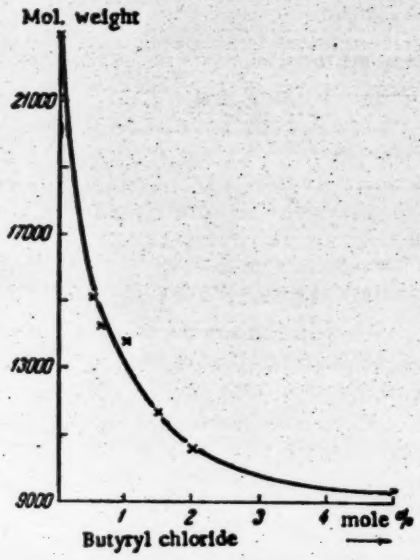

Fig. 4. Change in molecular weight of polyamide in relation to the addition of various amounts of butyryl chloride (the polymer was obtained by removal from solution)

Consequently, a change in the ratio of the starting materials had practically no effect on the molecular weight of the polyamides formed. It is interesting to compare this feature of nonequilibrium polycondensation with the fact that equilibrium polycondensation of the dicarboxylic acids themselves with diamines shows the dependence illustrated in Fig. 2, where the great effect of an excess of one of the starting materials is clearly shown. For comparison, the same figure shows data which we obtained for nonequilibrium polycondensation.

In any case, the factor leading to the cessation of reaction and stopping chain growth was the formation of a polyamide film at the boundary of the two phases. The starting materials could not diffuse through the film formed and therefore the reaction stopped long before complete exhaustion of the starting materials. Consequently, the effect of an excess of this or that component was of no importance. The situation was different in the case of equilibrium polycondensation where the reaction proceeded in a homogeneous melt and due to this the starting materials taken were able to react completely.

In connection with the results obtained, it was interesting to examine how the molecular weight in non-equilibrium polycondensation would be affected by the addition of monofunctional substances of the same chemical nature as the starting materials of the main reaction. For this purpose, we investigated the effect of adding butyryl chloride to a benzene solution of the original acid chloride.

As can be seen from this figure, the addition of butyryl chloride led to a considerable fall in the molecular weight of the polyamide formed. To convince ourselves of the reliability of this result and exclude the effect of chance, we carried out this reaction with the addition of n-butylamine to an aqueous solution of hexamethylene-diamine. Here, the addition also had a considerable effect on the molecular weight of the polyamide (cf. Figs. 3 and 4). With an increase in the amount of n-butylamine, the molecular weight of the polyamide obtained fell.

Such a difference in the behavior of monofunctional and difunctional substances in this reaction may only be explained on the basis of the chain-growth mechanism that occurs in this case.

The presence of excess of one of the starting materials does not lead to a loss in reactivity of the terminal groups of the polymer forming, as is shown below:

$$\ldots\text{—NH}(CH_2)_6NH_2 + ClCO(CH_2)_4COCl \rightarrow$$
$$\rightarrow \ldots\text{—NH}(CH_2)_6NHCO(CH_2)_4COCl + HCl,$$
$$\ldots\text{—CO}(CH_2)_4COCl + NH_2(CH_2)_6NH_2 \rightarrow$$
$$\rightarrow \ldots\text{—CO}(CH_2)_4CONH(CH_2)_6NH_2 + HCl$$

Therefore, the terminal groups do not lose their capacity to react with the other starting material and thus the chain grows further until its growth ceases as a result of other factors. When monofunctional substances are added, they close off the reactive terminal groups, as shown below:

$$\ldots\text{—NH}(CH_2)_6NH_2 + RCOCl \rightarrow \ldots\text{—NH}(CH_2)_6NHCOR + HCl,$$
$$\ldots\text{—CO}(CH_2)_4COCl + RNH_2 \rightarrow \ldots\text{—CO}(CH_2)_4CONHR + HCl.$$

Thus a polymer with such unreactive groups at both ends loses its capacity for further growth. Here the fall in molecular weight depends directly on the amount of monofunctional substance added.

These results indicate the essential difference between equilibrium and non-equilibrium polycondensations. In these two cases the effect of excess of the starting materials is different, while the effect of adding a monofunctional substance is the same and lowers the molecular weight.

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SYNTHESIS AND REARRANGEMENTS IN THE THIAZOLINIMINE SERIES

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(Presented by Academician I. L. Knunyants February 24, 1959)

In the condensation of thiourea or substituted thioureas with α-halocarbonyl compounds, derivatives of 2-aminothiazole or thiazolinimine are formed.

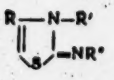
On the example of the condensation of substituted 2-mercaptoimidazoles with α-haloketones, it was shown that the formation of imidazo-(2, 1-b)-thiazoles proceeded through the intermediate stage of S-β-carbonyl compounds [1, 2].

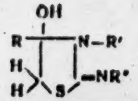
In the present work we studied the condensation of α-haloketones with symmetrical diaryl- and arylacylthioureas and also investigated the rearrangements we observed in the cyclic compounds obtained.

We confirmed that the course of the reaction depended on the presence of hydrogen ions in the reaction medium. If the hydrogen halide formed was bound with triethylamine, then we obtained 4-hydroxythiazolidine derivatives, which lost water when dissolved in aqueous or alcoholic hydrochloric acid. The intermediate hydroxy compounds were unstable, especially in those cases when they were obtained from diarylthioureas. For example, by condensation of chloroacetone with thiocarbanilide in methylene chloride solution in the presence of triethylamine at room temperature we obtained a compound, whose elementary analysis, hydroxyl content and IR spectrum showed that it was 2-phenylimino-3-phenyl-4-methyl-4-hydroxythiazolidine (Table 1, Ia). On heating, this substance lost water and was obtained from chloroacetone and thiocarbanilide [3] in alcohol solution without the addition of base. A mixture of (I) and (Ia) showed depression of melting point only in a sealed capillary. By condensation of symmetrical ditolyl- and diphenetidylthiourea with chloroacetone it was impossible to obtain intermediate hydroxy compounds and we obtained directly 2-tolylimino-3-tolyl-4-methylthiazoline (II) and 2--p-ethoxyphenylimino-3-p-ethoxyphenyl-4-methylthiazoline (III), which were also formed by condensation of the components without binding the hydrogen chloride with a base.

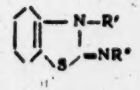
The intermediate substances obtained by condensation of α-haloketones with N-aryl-N'-acylthioureas were found to be more stable. On a series of examples, it was shown that 4-hydroxythiazolidine compounds were obtained in the presence of triethylamine both in methylene chloride solution at room temperature and in alcohol solution with heating. When treated with hydrochloric acid in the cold or heated with an alcohol solution of hydrogen chloride, they lost water and were converted into the corresponding thiazoline compounds, which differed sharply in melting point in most cases. From chloroacetone and benzoylphenylthiourea we obtained 2-benzoylimino-3-phenyl-4-methyl-4-hydroxythiazolidine (IVa) and 2-benzoylimino-3-phenyl-4-methylthiazoline (IV), from chloroacetone and phenyl-p-nitrobenzoylthiourea, 2-(p-nitrobenzoylimino)-3-phenyl-4-methyl-4-hydroxythiazolidine (Va) and 2-(p-nitrobenzoylimino)-3-phenyl-4-methylthiazoline (V) and an analogous pair of substances (VI and VIa) from chloroacetone and phenylacetylthiourea; from α-chlorocyclohexanone and phenylacetylthiourea we obtained 2-acetylimino-3-phenyl-4-hydroxy-4, 5-cyclotetramethylenethiazolidine (XIa) and 2-acetylimino-3-phenyl-4, 5-cyclotetramethylenethiazoline-4 (XI); from ω-bromoacetophenone and phenylbenzoylthiourea, we obtained 2-benzoylimino-3, 4-diphenyl-4-hydroxythiazolidine (VIIa) and 2-benzoylimino-3, 4-diphenylthiazoline-4 (VII). In all cases, the presence of a hydroxy group in the thiazolidine was demonstrated by the IR spectra and also by direct determination of the hydroxy group by Zerevitinov's method. Here the 4-hydroxythiazolidine compound (XIa) gave two moles of methane, which corresponds to the behavior of alcohols with

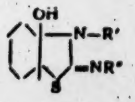
TABLE 1



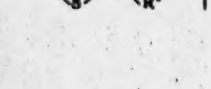


No	R	R'	R"	M.p., in °C	Calculated %				Found %				No.	M.p., in °C	Calculated %					Found %				
					C	H	N	S	C	H	N	S			C	H	N	S	OH	C	H	N	S	OH
I	CH_3	p-C_6H_5	p-C_6H_5	138—139	72,4	5,28	10,52	12,02																
II	CH_3	p-$CH_2C_6H_5$	p-$CH_2C_6H_5$	111—113	73,8	6,31	9,55	10,89	73,33	6,00	9,37	11,04												
III	CH_3	p-C_6H_5O-C_6H_4	p-$C_6H_5OC_6H_4$	162—163	68,00	6,28	7,93	9,08	67,80	6,13	7,82	9,01												
IV	CH_3	C_6H_5	COC_6H_5	156—158	69,37	4,8	9,5	10,89	69,24	4,85	9,48	10,70	IVa	158—160	65,34	5,16	8,97	10,26	5,44	65,86	5,37	8,88	9,93	5,75
V	CH_3	C_6H_5	$COC_6H_4NO_2$-p	184—185	60,16	3,86	12,38	9,45	60,14	3,84	12,38	9,67	Va	160—162	57,1	4,23	11,77	8,97	4,06	57,33	4,28	11,58	9,14	4,48
VI	CH_3	C_6H_5	$COCH_3$	182—183									VIa	132,5—133,5	57,58	5,64	11,19	12,81	6,8	57,51	5,71	11,30	12,99	6,34
VII	C_6H_5	C_6H_5	COC_6H_5	203—204	74,13	4,52	7,86	8,99	74,10	4,55	7,77	9,10	VIIa	155,5—156,5	70,55	4,84	7,48	8,56	4,54	70,30	4,67	7,74	8,53	3,58





No.	R'	R"	M.p., in °C	Calculated %				Found %				No.	M.p., in °C	Calculated %					Found %				
				C	H	N	S	C	H	N	S			C	H	N	S	OH	C	H	N	S	OH
IX	C_6H_5	COC_6H_5	204—205	71,85	5,42	8,38	9,59	72,12	5,38	8,30	9,40												
X	C_6H_5	$COC_6H_4NO_2$-p	157,5—159	63,31	4,51	11,08	8,45	63,36	4,62	11,00	8,55												
XI	C_6H_5	$COCH_3$	144,5—145,5	66,68	5,92	10,29	11,77	66,71	6,11	10,20	11,57	XIa	158—159	62,05	6,25	9,65	11,04	5,86	62,16	6,37	9,52		11,45
XII	C_6H_5	H	117—118	67,76	6,13	12,17	13,92	67,88	6,23	12,06													



No.	R	R'	R"	M.p., in °C	Calculated %				Found %			
					C	H	N	S	C	H	N	S
XIII	C_6H_5	C_6H_5	$COCH_3$	197,5—198,5	72,6	4,53	7,05	8,07	72,84	4,67	7,01	7,99
XIV	C_6H_5	H	H	196,5—197,5	74,13	4,52	7,86	8,99	74,07	4,41	7,83	8,77
XV	CH_3	CH_3	$COCH_3$	174—175	61,50	5,20	10,22	11,65	61,61	5,20	10,27	11,80
XVI	CH_3	CH_3	H	152—153	62,04	5,206	12,06	13,80	62,06	5,15	12,13	13,61

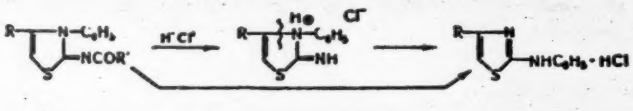
hydrogen at a tertiary α-carbon atom. Condensation of α-chlorocyclohexanone with phenylbenzoylthiourea in methylene chloride solution in the presence of triethylamine yielded a mixture of the hydroxy compound with the corresponding thiazoline (IX). On recrystallization and even more rapidly on treatment with hydrochloric acid, the elimination of water occurred with the formation of 2-benzoylimino-3-phenyl-4, 5-cyclotetramethylenethiazoline (IX). The intermediate compound could not be isolated in the reaction of phenyl-p-nitrobenzoylthiourea with α-chlorocyclohexanone. The instability of the 4-hydroxy compounds in these cases may be explained by the conformation of the cyclohexane nucleus, causing the approach of the hydrogen and hydroxyl to the trans position. A similar phenomenon was observed by Stevens for 4, 5-cyclotetramethylenethiazolinones-2 [4].

On heating for a few minutes with hydrochloric acid, the acyliminothiazolines (IV, V and VI) we obtained were hydrolyzed to 2-imino-3-phenyl-4-methylthiazoline-4 (m.p. 85 – 86°, acetyl derivative, m.p. 182 – 183°), which was described by Beyer [5]. If this imine was boiled with 20% hydrochloric acid for a few hours (or IV, V and VI boiled), then rearrangement occurred with the formation of 2-phenylamino-4-methylthiazole. We showed that the latter was identical with the compound obtained by Traumann's method [6] from chloroacetone and phenylthiourea. Compound VII was hydrolyzed to 2-imino-3, 4-diphenylthiazoline-4, which was obtained by Beyer from ω-thiocyanoacetophenone and aniline hydrochloride [5]. On prolonged boiling with hydrochloric acid, this imine rearranged into 2-phenylamino-4-phenylthiazole, which we identified with that described in the literature [5, 7].

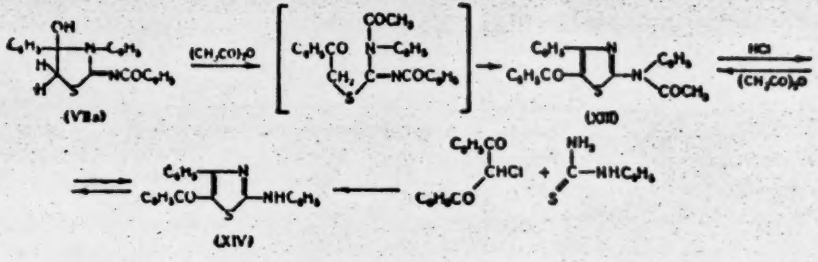
By heating ω-bromoacetophenone with phenylacetylthiourea in absolute alcohol we obtained 2-acetylimino-3, 4-diphenylthiazoline-4 (VIII). This compound was described by Beyer and was hydrolyzed to 2-imino-3, 4-diphenylthiazoline-4. However, in the presence of triethylamine, ω-bromoacetophenone and phenylacetylthiourea formed hydroxy compound IVa, which was obtained under the same conditions from chloroacetone and phenylbenzoylthiourea. Thus, during the course of the reaction the benzoyl appeared to have moved from the methylene group to the nitrogen of the thiourea residue and the acetyl from this nitrogen atom to the methylene group.

When heated with 20% hydrochloric acid, compound (IX), 2-p-nitrobenzoyl-3-phenyl-4, 5, 6, 7-tetrahydrobenzthiazoline (X) and 2-acetylamino-3-phenyl-4, 5, 6, 7-tetrahydrobenzthiazoline (XI) were hydrolyzed to 2-imino-3-phenyl-4, 5, 6, 7-tetrahydrobenzthiazoline (XII). On boiling for several days with 20% hydrochloric acid, this substance was converted into 2-phenylamino-4, 5, 6, 7-tetrahydrobenzthiazole (obtained by Indian authors by condensation of cyclohexanone with phenylthiourea in the presence of iodine [8]). It is interesting to note that in an attempt to prepare this substance by condensation of α-chlorocyclohexanone with phenylthiourea, (XII) was obtained.

We consider that the conversions described can be explained in the following way: the substituted thioureas in the iso form react with α-haloketones to form S-β-keto-substituted isothioureas, which rapidly undergo further conversions. The carbonyl oxygen abstracts a proton from the aminophenyl residue, which also forms an N – C bond to give 4-hydroxythiazolidine compounds, that readily lose water. The rearrangement of 2-imino-3, 4-substituted thiazolines on boiling with hydrochloric acid may be explained by the addition of a proton to the ring nitrogen, rupture of the 3, 4-bond and polarization of the molecule due to this with subsequent ring closure at the imino group nitrogen to form 2-phenylamino-4-substituted thiazoles.



We attempted to acetylate the hydroxyl group of 4-hydroxythiazolidine compounds with acetyl chloride or acetic anhydride. However, O-acetylation did not occur and there was either elimination of water, as in the case of (IVa) and (Va) and the formation of (IV) and (V), or rearrangement involving rupture of the 3, 4-bond. Thus, when heated with acetic anhydride, (VIIa) formed 2-(N-phenyl-N-acetyl)-amino-4-phenyl-5-benzoylthiazole (XIII), in which the presence of a keto group was demonstrated by means of the IR spectrum. This substance was hydrolyzed by 20% hydrochloric acid with the formation of 2-phenylamino-4-phenyl-5-benzoylthiazole (XIV), whose structure we proved by synthesis from dibenzoylchloromethane and phenylthiourea. (XIV) was acetylated to (XIII) by acetic anhydride. Similar conversions occurred with (VIa), which reacted with acetic anhydride to give not only (VI), by loss of a molecule of water, but also 2-(N-phenyl-N-acetyl)-amino-4-methyl-5-acetylthiazole (XV). The latter was hydrolyzed to 2-phenylamino-4-methyl-5-acetylthiazole (XVI). The structure



of (XVI) was proved by synthesis from diacetylchloromethane and phenylthiourea. The same substance (XVI) was obtained from phenylacetylthiourea and chloroacetone in alcohol in the presence of triethylamine. These conversions may be explained in the following way. In the action of acetic anhydride on (VIIa) and (VIa), opening of the thiazolidine ring occurred at the 3, 4-bond with the formation of an S-β-keto derivative of isothiourea and acetylation of the secondary amino group. In these keto compounds the hydrogen atoms of the methylene group had a high lability and reacted with the carbonyl of the acyl residue at the imino group forming (XIII) and (XV).

The reactions investigated showed that condensation of α-haloketones with N-phenyl-N'-acylthioureas proceeds through 4-hydroxythiazolidine derivatives and that these compounds, like 2-iminothiazolines-4, are very labile and capable of rearrangements involving opening of the hetero ring.

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* Original Russian pagination. See C.B. Translation.

THE ADDITION OF LITHIUMDIETHYL- AND LITHIUMDIBUTYLAMIDES TO VINYLACETYLENE AND VINYLALKYLACETYLENES

A. A. Petrov and V. A. Kormer

(Presented by Academician B. A. Arbuzov March 4, 1959)

There is very little information inthe literature on the interaction of vinylacetylene hydrocarbons with amines [1 — 3]. Only the addition of ammonia and certain amines to vinylacetylene has been investigated and the reaction was carried out at 100° at elevated pressure [1] or on a heterogeneous catalyst at 250° [2]. This yielded allene amines (I) or the products of thier isomerization, acetylene amines (II).

$$HC\equiv C-CH=CH_2 \xrightarrow{R_2NH} CH_2=C=CHCH_2NR_2 \quad (I)$$

$$CH_3-C\equiv C-CH_2NR_2 \quad (II)$$

In this work it was shown that the adducts of amines (diethyl- and dibutylamines) to vinylacetylenes (vinylacetylene, vinylmethylacetylene and vinylethylacetylene) were obtained by water treatment of the products from adding lithiumdialkylamides to these hydrocarbons. The lithiumdialkylamides reacted with vinylacetylenes at room temperature and normal pressure. This reaction has not been described in the literature.

Depending on the nature of the vinylacetylene and the amine, various products were obtained from the reaction.

Vinylacetylene formed amines (III) with a terminal acetylene group (20% yield in the case of diethylamine) without any side processes.

$$HC\equiv C-CH=CH_2 \xrightarrow{{}^tR_2N-Li} HC\equiv C-CHLi-CH_2NR_2 \xrightarrow{H_2O} \rightarrow HC\equiv C-CH_2-CH_2NR_2 \quad (III)$$

Vinylmethylacetylene gave predominantly the dimer (IV) in about 40% yield and polymers (25 — 30% yield). A very small amount of amines (5%) was formed and they had different structures depending on the nature of the amide: in the case of lithiumdiethylamideaddition, an amine with a terminal acetylene grouping (V) was formed and in the case of lithiumdibutylamide, an amine of the allene type (VI).

$$CH_3-C\equiv C-CH=CH_2 \rightarrow \begin{cases} H-C\equiv C-CH=CH-CH_2-CH(CH_3)-CH_2-C\equiv CH & (IV) \\ HC\equiv C-CH_2-CH_2-CH_2-NR_2 & (V) \\ R-CH=C=CH-CH_2-NR_2 & (VI) \end{cases}$$

With lithiumdialkylamides, vinylethylacetylene gave amines of the allene type (VI) in 45 — 55% yield. In this case the amount of dimer did not exceed 10%.

The structure of the amines was demonstrated first of all by their infrared spectra. The spectra of amines obtained from vinylacetylene and vinylmethylacetylene with lithiumdiethylamide showed only bands of a terminal acetylene group (3300 and 2123 cm^{-1}), while the bands of allene and 1, 3-diene systems were absent

(Fig. 1, 1 and 2). The spectra of amines obtained from vinylmethylacetylene and dibutylamine and also all the amines from vinylethylacetylene had only the bands of an allene system at 1960 cm^{-1} (Fig. 1, 3 and 4). Amines obtained from vinylacetylene and vinylmethylacetylene with diethylamine were found to be identical in constants to 1-diethylaminobutyne-3 and 1-diethylaminopentyne-4, respectively, which are described in the literature [4]. It should be noted that isomeric amines of the type $HC \equiv C - CH(NR_2) - R$, which could arise by a different order of addition of the lithiumdialkylamides to the vinylacetylenes, have quite different constants [4].

The structure of the amines obtained from vinylethylacetylene were confirmed by their hydrogenation on colloidal palladium to the corresponding dialkylhexylamines, which were prepared by another method for comparison. The isomeric amines of the type $C_2H_5 - CH(NR_2) - C_3H_7$ have considerably lower boiling points [5].

On catalytic hydrogenation on colloidal palladium, the dimer of vinylmethylacetylene added 5 molecules of H_2 with the formation of 4-methylnonane and, consequently, had an open chain of carbon atoms. It was shown to contain two terminal acetylene bonds by the usual method [6].

The infrared spectrum of the dimer (Fig. 1, 5) showed two bands corresponding to terminal acetylene bonds, one of which (2100 cm^{-1}) was conjugated with a double bond. The band at 1616 cm^{-1} correspond to the conjugated double bond. The presence of absorption in the region of 964 cm^{-1} indicated that the double bond contained the grouping $-CH = CH-$.

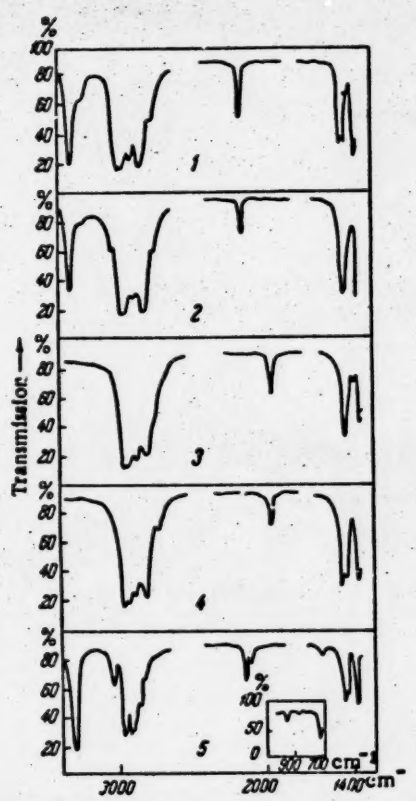

Fig. 1. Infrared transmission spectra: 1) 1-diethylaminobutyne-3, 2) 1-diethylaminopentyne-4, 3) 1-dibutylaminopentadiene-2, 3, 4) 1-diethylaminohexadiene-2, 3, 5) 6-methylnonene-3-diyne-1, 8.

All these data made it possible to assign the formula of 6-methylnonene-3-diyne-1, 8 (VI) to the dimer. Judging by spectral data (frequencies found: 969, 2092, 2127, 3024, 3290 cm^{-1}), the dimer of vinylethylacetylene had an analogous structure.

It is most probable that the dimers were formed as a result of addition of the metallation products to the vinylalkylacetylenes with transposition of the multiple bonds to the end of the chain under the effect of the lithiumdialkylamides. The constants of the substances obtained are given in Table 1.

Thus, as a result of the given investigation it was established that lithiumdialkylamides added to vinylacetylenes similarly to alkyllithiums, i.e. the radical entered position 4 [7]. In both cases the reaction probably proceeded by a radical mechanism.

EXPERIMENTAL

The lithiumdialkylamides were prepared by the action of appropriate amines (0.5 – 0.7 mole) on ether solutions of methyllithium or ethyllithium (0.5 – 0.6 mole) [8]. When vinylacetylene hydrocarbons (0.25 mole) were introduced into these solutions, a vigorous reaction was observed with a rise in temperature. After standing for 1 – 24 hours (1 – 2 hours in the case of vinylethylacetylene and 12 – 24 hours for the rest), the mixture was treated with water, dried over aluminum oxide and distilled, at first at normal pressure and then in vacuum. The amines were freed from hydrocarbons by solution in dilute hydrochloric acid with subsequent liberation with alkali. The analytical data for the newly prepared substances are given in Table 2.

Hydrogenation of 1-diethylaminohexadiene-2, 3. During exhaustive hydrogenation, 3.1 g of amine absorbed

TABLE 1

Substance	B.p., °C (20 mm)	d_4^{20}	n_D^{20}	MR found	MR calc.
$HC\equiv C-CH_2-CH_2N(C_2H_5)_2$*	48	0,8031	1,4388	40,99	41,08
$HC\equiv C-CH_2-CH_2-CH_2N(C_2H_5)_2$**	60,5—61,5	0,7901	1,4378	46,24	45,70
$CH_3-CH=C=CH-CH_2N(C_4H_9)_2$	123—124	0,8119	1,4588	65,75	65,24
$C_2H_5-CH=C=CH-CH_2N(C_3H_7)_2$	85—86	0,8111	1,4554	51,30	51,39
$C_2H_5-CH=C=CH-CH_2N(C_4H_9)_2$	136—136,5	0,8150	1,4558	69,80	69,86
$HC\equiv C-CH=CH-CH_2-CH(CH_3)-CH_2-C\equiv CH$	71—72	0,8346	1,4780	44,84	43,91

* B.p. 143—143.5°/765 mm, 85°/110 mm. Literature data [4]: b.p. 139—142°/680 mm, 85°/110 mm, n_D^{18} 1.4390.

** B.p. 76°/40 mm. Literature data [4]: b.p. 76°/40 mm, n_D^{20} 1.4380.

TABLE 2

Substance	Found % C	Found % H	Found % N	Calculated % C	Calculated % H	Calculated % N
$CH_3-CH=C=CH-CH_2N(C_4H_9)_2$	79,71 79,75	12,94 13,07	7,52	79,93	12,90	7,17
$C_2H_5-CH=C=CH-CH_2N(C_2H_5)_2$	78,23 78,41	12,46 12,53	8,99 9,50	78,36	12,46	9,14
$C_3H_7-CH=C=CH-CH_2N(C_4H_9)_2$	80,48 80,47	12,90 12,86	7,14 6,88	80,31	13,00	6,69
$HC\equiv C-CH=CH-CH_2-CH(CH_3)-CH_2-C\equiv CH$*	90,91 90,83	9,12 9,12	— —	90,85	9,15	—

* Found: mol. weight 131.3, 132.9; amount of $-C\equiv CH$ 1.98, 1.97%.
Calculated: mol. weight 132.2; amount of $-C\equiv CH$ 2.00%.

980 ml of H_2 (757 mm, 18°), i.e., about 100% of theoretical. The reaction mixture yielded diethylhexylamine (2.8 g) with b.p. 179—180°/750 mm, 75.5—76.5°/20 mm, d_4^{20} 0.7688, n_D^{20} 1.4252. The same amine obtained from diethylamine and hexyl bromide had the constants: b.p. 179—180°/750 mm, d_4^{20} 0.7676, n_D^{20} 1.4242. The infrared spectra of the two amines did not differ.

Hydrogenation of 1-dibutylaminohexadiene-2, 3. During exhaustive hydrogenation, 4.15 g of the amine absorbed 978 ml of H_2 (745.5 mm, 16°), i.e., about 100% of theoretical. The reaction mixture yielded dibutylhexylamine (3.8 g) with b.p. 129—130°/20 mm, d_4^{20} 0.7864, n_D^{20} 1.4360. The same amine obtained from dibutylamine and hexyl bromide had: b.p. 129—130°/20 mm, d_4^{20} 0.7853, n_D^{20} 1.4350. The spectra of the two samples of amine were the same.

Hydrogenation of dimer of vinylmethylacetylene. During exhaustive hydrogenation, 3.3 g of dimer absorbed 2966 ml of H_2 (766.3 mm, 19°), which corresponds to 98% of theoretical. We obtained 2.9 g of 4-methylnonane with b.p. 164—165°/750 mm, 82—82.5°/50 mm, d_4^{20} 0.7350, n_D^{20} 1.4148. These constants are extremely close to those given in the literature for 4-methylnonane [9]. The infrared spectra of the hydrocarbons and authentic 4-methylnonane did not differ.

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SYNTHESIS OF HIGHER KETONES BY OXIDATION OF PARAFFINIC HYDROCARBONS

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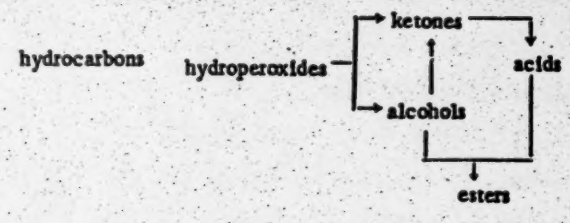
In studying the liquid phase oxidation of paraffinic hydrocarbons we noticed that at temperatures of 120 – – 160° in the first stages of the oxidation, the formation of carbonyl compounds proceeded at a considerable rate, exceeding the rate of formation of alcohols and acids.

Guided by ideas on the order in which oxygen-containing compounds of various classes are formed during oxidation of hydrocarbons (see scheme) [1, 2], it could be considered that in this case the ketones were largely formed directly from hydroperoxides. This observation served as the basis for an investigation aimed at determining the possibility of a directed synthesis of higher ketones by liquid-phase oxidation of paraffinic hydrocarbons.



To solve the problem we studied the effect of reaction conditions (temperature, oxygen content of the oxidizing gas and oxidation time) and also the effect of various additives on the oxidation rate and composition of the products obtained.

We oxidized a fraction of synthetic paraffinic hydrocarbons (hydrogenated) boiling in the range 105 – 130° at 1 mm Hg and consisting of hydrocarbons with from 16 to 18 carbon atoms. This fraction had an iodine number of 2.3, d_4^{20} 0.7722 and n_D^{20} 1.4366.

The apparatus used and the oxidation and analysis procedures were described previously [3]. The charge of hydrocarbons to be oxidized was 60 g for each experiment and the consumption of oxidizing gas was 1000 liter/kg·hour for oxygen – nitrogen mixtures and 200 liter/kg·hour for oxygen.

Studying the effect of temperature (see Table 1) showed that raising the temperature to 165° considerably increased the extent of conversion of original hydrocarbons. A further increase in the temperature to 185° had hardly any effect on the extent of conversion. The greatest yield of ketones was observed at temperatures of 120 – 140° (Table 1). In oxidation of the hydrocarbons with an oxygen – nitrogen mixture containing 3.5% of oxygen and with oxygen, the same rules were observed.

On studying the effect of concentration of oxygen in the oxidizing gas, it was established that increasing the latter from 3.5 to 21% led to a reduction in the fraction of ketones in the reaction products (see Table 2).

TABLE 1

Effect of Temperature on Composition of Oxidation Products From Paraffinic Hydrocarbons (oxidation with air, oxidation time 4 hours)

Temperature, °C	Analysis of oxidate					Amount of oxygen-containing compounds formed			
	peroxide number	acid number	ester number	hydroxyl number	carbonyl number	total, mmole/g	including, in mole %		
							acids	ketones	alcohols
130	2,0	3,4	5,4	6,4	12,5	0,59	26,8	37,6	35,6
140	9,9	5,0	13,0	36,7	1,24	21,4	52,6	26,0	
165*	[illegible]	[illegible]	[illegible]	53,0	52,8	4,02	31,3	23,5	45,2
175	39,2	53,6	41,7	51,0	4,10	36,1	22,2	41,7	
185	—	27,3	51,5	46,5	58,5	4,21	33,5	24,9	41,6

* Gas consumption 500 liter/kg hour.

TABLE 2

Effect of Oxygen Concentration in the Oxidizing Gas on the Composition of the Oxidation Products from Paraffinic Hydrocarbons

Experiment No.	Concentration of oxygen in oxidizing gas, %	Analysis of oxidate					Amount of oxygen-containing compounds formed			
		peroxide number	acid number	ester number	hydroxyl number	carbonyl number	total, mmole/g	including, in mole %		
								acids	ketones	alcohols
Temperature 120°, oxidation time 4 hours										
1	3,5	4,2	4,1	0,0	5,0	13,6	0,406	18,2	60,0	21,8
2	21,0	2,0	3,5	5,4	6,4	12,5	0,593	26,8	37,6	35,6
3	100,0	—	4,4	1,1	12,0	22,8	0,740	13,4	55,0	31,6
Temperature 120°, oxidation time 6 hours										
4	3,5	7,6	4,9	0,0	0,0	17,85	0,410	22,0	78,0	0,0
5	21,0	6,1	5,0	8,3	0,3	18,6	0,727	32,9	45,7	21,4
6	100,0	—	6,3	0,0	14,5	25,8	0,834	13,5	55,4	31,1

TABLE 3

Effect of Oxidation Time on the Composition of the Oxidation Products From Paraffinic Hydrocarbons

Oxidation time, hours	Analysis of oxidate					Amount of oxygen-containing compounds formed			
	peroxide number	acid number	ester number	hydroxyl number	carbonyl number	total, mmole/g	including, in mole %		
							acids	ketones	alcohols
4	10,3	5,2	8,1	20,0	35,2	1,37	17,4	46,0	36,6
6	6,3	7,0	7,0	21,3	28,2	1,25	19,9	40,2	39,9
8	3,5	9,7	15,7	24,0	35,6	1,76	24,8	34,0	41,2

Simultaneously with this, the extent of conversion of the original hydrocarbons increased. The greatest yield of ketones was observed at a low concentration of oxygen in the oxidizing gas mixture. However, the possibility of finding other oxidation conditions, making it possible to obtain ketones in high yield, was not excluded. Thus,

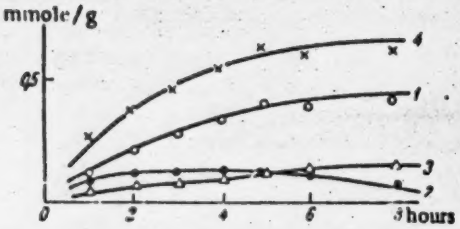


Fig. 1. Kinetics of oxygen-containing compound accumulation (oxidation with oxygen at 120°), 1) carbonyl compounds, 2) hydroxyl compounds, 3) acids (free and bound), 4) total content of oxygen-containing compounds.

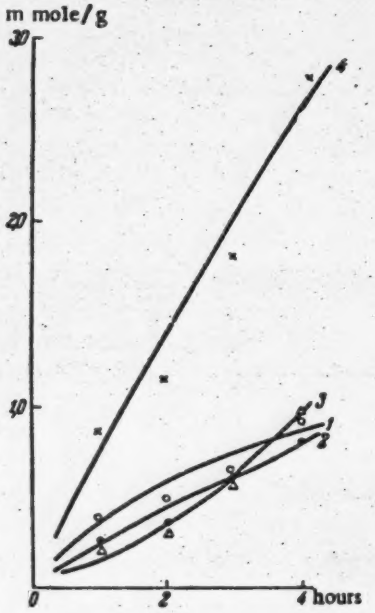


Fig. 2. Kinetics of oxygen-containing compound accumulation (oxidation with oxygen at 140°). 1) Carbonyl compounds, 2) hydroxyl compounds, 3) acids (free and bound), 4) total content of oxygen-containing compounds.

for example, reducing the specific consumption of oxidizing gas from 1000 liter/kg·hour to 200 liter/kg·hour and the use here of oxygen as the oxidizing gas made it possible to obtain a ketone yield of about 55 mole% on the paraffins reacting (see Table 2).

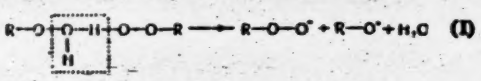
The effect of the oxidation time of paraffinic hydrocarbons on the composition of the oxidate was studied for oxidation by an oxygen–nitrogen mixture containing 3.5% oxygen at a temperature of 140° (Table 3).

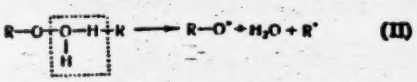
Data in Table 3 show that with an increase in oxidation time, the extent of oxidation of the original hydrocarbons increased and the ketone yield fell. Depending on the reaction conditions, the maximum ketone yield was observed at various oxidation times. Thus, with oxidation by air at 140°, the optimal oxidation time was 3 — 4 hours.

At a temperature of 120° the process of hydrocarbon oxidation was slowed after a certain time on reaching a certain limiting degree of conversion, which depended on the reaction conditions (see Fig. 1). With oxidation by oxygen, this state set in when a degree of conversion of 10–15 mole% was reached. Subsequently there was some increase in the fraction of ketones and acids due to oxidation of the alcohols in the reaction zone (see Fig. 1 and Exps. No. 1, 4, 2 and 5, Table 2). In this case it is probable that oxidation of the alcohols could have occurred in the system with the oxidation of hydrocarbons slowed.

The process of hydrocarbon oxidation proceeds by a free radical chain mechanism and is a process with degenerate branching of the chains. The presence of autoacceleration of hydrocarbon oxidation reaction at comparatively low temperatures is caused by the decomposition of hydroperoxides. The rate of oxidation depends to a large extent on the rate of formation and concentration of free radicals in the reaction zone.

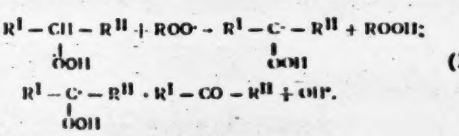
Bimolecular decomposition of hydroperoxide [4] by the reactions


(I)


(II)

leads to chain branching. In a system with reaction build-up, decomposition of hydroperoxides may also proceed [1] by interaction with a radical by reactions III.

The slowing of the hydrocarbon oxidation reaction which we observed (at 120°) was probably due to the fact that the concentration of free radicals responsible for the oxidation reaction fell sharply or their formation ceased completely.


(III)

At higher temperatures slowing of the reaction was not observed and oxidation of the hydrocarbons proceeded to a considerable degree of conversion (35 – 40 mole %). However, in this case, together with ketones there was accumulation of a large amount of alcohols, esters, acids and other oxygen-containing compounds (Fig. 2).

An attempt to increase the yield of ketones by the introduction of $KMnO_4$, $FeSO_4$ and other salts of variable valence metals did not lead to positive results. Therefore, subsequently our attention was directed to determining the possibility of influencing the rate of decomposition of hydroperoxides by reactions (I) and (II). It could be expected that if these reactions were responsible for branching, the rate of oxidation and the limiting extent of oxidation could be increased by introducing substances capable of forming a hydrogen bond with the oxygen of hydroperoxide [5]. To test this hypothesis experimentally we carried out experiments with the addition of monocarboxylic acids (formic, butyric and caproic) and dibasic aliphatic acid (oxalic, succinic, adipic and sebacic) and also of hydrogen bromide, chloride and sulfide. The investigation showed that in a series of cases the introduction of mono- and dibasic acids increased the fraction of ketones, due to a decrease in the formation of side-products (alcohols and acids) and the oxidation rate decreased somewhat at the same time. The introduction of hydrogen bromide, chloride and sulfide into the reaction zone had no essential effect on the extent of hydrocarbon conversion or the ratio between the the main products in the oxidate.

The experimental data obtained indicate that under the conditions we studied the formation of free radicals responsible for branching proceeds mainly through reaction (III) and not reactions (I) and (II).

For investigating the composition of the carbonyl compounds obtained by oxidation of paraffinic hydrocarbons, the oxidate (acid number 5.4; ester no. 2.6; hydroxyl no. 5.4 and carbonyl number 25.5) was put through a separation procedure including the following operations: 1) chromatographic separation of unreacted hydrocarbons from oxygen-containing compounds; 2) hydrolysis of the latter with alkali to isolate the fatty acids through their salts; 3) esterification of the alcohols with boric acid and 4) vacuum distillation of carbonyl compounds from the boric esters of the alcohols. The distillate obtained had a carbonyl number of 201.0, acid and ester numbers of zero and a hydroxyl number of 3.1.

The carbonyl compounds isolated were a mixture of higher aliphatic ketones.

Thus, as a result of the investigation it was shown that higher aliphatic ketones could be obtained by direct oxidation of paraffinic hydrocarbons in yields of about 65 mole % on the hydrocarbon converted. Here the degree of conversion of the hydrocarbons was 10 – 15 mole %. Oxidation under conditions producing a higher degree of conversion of the hydrocarbons led to the formation of considerable amounts of alcohols and acids in addition to ketones.

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SYNTHESIS OF NICOTINIC ACID AND ITS AMIDE THROUGH NICOTINONITRILE

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(Presented by Academician M. M. Shemyakin October 20, 1958)

Nicotinic acid and its amide have found wide application as the antipellagra vitamin "PP" and for the synthesis of many important physiologically active substances [1]. Nicotinic acid is also used as an efficient growth accelerator for cotton plants [2].

Despite the great and ever increasing demand for nicotinic acid and its amide, present day industrial methods for their preparation are based on the oxidation of pyridine derivatives to the acid with such oxidants as potassium permanganate, nitric acid and potassium bichromate [3] and subsequent conversion of the acid into the amide [4]. The yield of nicotinic acid thus varies over the range 45 – 60% of theoretical and the amide yield is about 60% of the acid taken, i.e., not more than 35% on the original alkylpyridine. Attempts to use atmospheric oxygen as the oxidant gave insignificant yields [5].

We prepared nicotinic acid and nicotinamide by hydrolysis of nicotinonitrile, formed in high yield by oxidative ammonolysis of β-picoline on vanadium catalysts. The possibility of vapor phase catalytic ammonolysis of β-picoline with the formation of nicotinonitrile has been reported previously in certain patents [6]. In this work we used a procedure developed previously for the oxidative ammonolysis of alkylbenzenes [7].

β-Picoline, isolated from an industrial β-picoline fraction [8], had the following constants: b.p. 142–143°, d_4^{20} 0.9560, n_D^{20} 1.5062.

Oxidative ammonolysis of β-picoline was carried out in a flow type reactor. The catalyst used was granulated tin vanadate. Air was used as oxidant; the ammonia was introduced into the reaction zone as a 20% aqueous solution. The contact time was 0.2–0.6 sec and the volume rate of starting material imput was 0.04–0.07 liter per liter of catalyst per hour.

The reaction products were passed successively through two flasks 3 liters in volume, cooled with cold water, two bubblers with water and a scrubber sprayed with 5% alkali solution.

The nicotinonitrile and unreacted β-picoline were extracted with ether. The extract was dried over fired sodium sulfate and fractionally distilled. The bulk of the nicotinonitrile distilled at 190–192°/695 mm. m.p. 49–50°. On hydrolysis with water under pressure with a few drops of aqueous ammonia, the nicotinonitrile gave nicotinamide with m.p. 129–130° and nicotinic acid with m.p. 232–234°. The yield of nicotinamide and nicotinic acid depended on the reaction conditions for nicotinonitrile hydrolysis. It should be noted that hydrolysis of nicotinonitrile occurred even on normal boiling with water. By changing the hydrolysis conditions, it was possible to obtain a quantitative yield of nicotinic acid or its amide.

The gaseous reaction products (hydrogen cyanide, carbon monoxide and carbon dioxide) were analyzed by a procedure developed previously [9].

In all the experiments the residue of the reaction liquid was evaporated and neutralized in pH 3.6 with hydrochloric acid to give a further amount (4–5 of theoretical) of nicotinic acid with m.p. 233–234°. It is possible that it was formed in the collection system due to the ready hydrolyzability of nicotinonitrile.

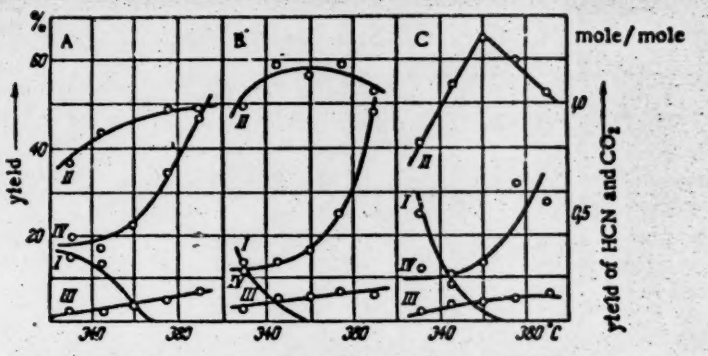

Fig. 1. Oxidative ammonolysis of β-picoline: A) 5-fold excess of ammonia, B) 10-fold excess of ammonia, C) 20-fold excess of ammonia. I) Unreacted β-picoline, II) nicotinonitrile, III) hydrocyanic acid, IV) carbon dioxide.

As a result of preliminary experiments it was established that the contact time did not have a noticeable effect on the oxidative ammonolysis of β-picoline over the temperature interval investigated and further experiments were carried out at a contact time of 0.4 sec.

The reaction temperature had a considerable effect on the yield of nicotinonitrile (Fig. 1). Increasing it from 310 to 370° produced an increase in the nicotinonitrile yield. A further increase in the temperature (up to 400°) led to a decrease in the yield; simultaneously there was a sharp increase in carbon dioxide formation. It should be noted that this effect of temperature on the catalytic oxidative ammonolysis of β-picoline was characteristic of all the experiments, despite the fact that the ratio of starting materials, contact time and volume rate were varied over wide limits. From this we can surmise that at high temperatures (370°), in addition to oxidative ammonolysis of β-picoline, there was also deep oxidation leading to the formation of carbon dioxide.

As Fig. 1 shows, a change in the amount of ammonia introduced into the reaction zone also had an effect on the course of oxidative ammonolysis of β-picoline. In the series of experiments described, the highest yield of nicotinonitrile (65.0% of theoretical) and the least carbon dioxide formation were observed at a 20-fold (with respect to theory) excess of ammonia. Consequently, excess of ammonia suppressed the deep oxidation processes.

The yield of hydrocyanic acid was insignificant and, depending on the experimental conditions, varied over the range 0.05 – 0.1 mole per mole of β-picoline taken.

Thus, the use of thecatalytic oxidative ammonolysis of β-picoline makes it possible to obtain nicotinic acid in a total yield of more than 65% or nicotinamide in a yield of more than 60% on the starting material taken. The method does not require the use of difficultly available oxidants. For the synthesis of nicotinonitrile it is possible to use a normal apparatus, employed for the catalytic oxidation of hydrocarbons.

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ALKYLATION OF BENZENE AND ITS DERIVATIVES BY ISOPROPYL ALCOHOL OVER AN ALUMINOSILICATE CATALYST AT ATMOSPHERIC PRESSURE

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The alkylation of benzene and its derivatives attracts considerable attention from investigators. This is connected with the ever increasing importance of various alkyl products.

As is known, aluminosilicate catalysts are widely used in catalytic reactions at the present time. However, vapor-phase alkylation at atmospheric pressure in the presence of these catalysts has not been investigated sufficiently as yet.

We studied the alkylation of benzene, toluene, phenol, chloro- and bromobenzenes and nitrobenzene by isopropyl alcohol under the conditions mentioned above.

As a result we obtained cumene, which is a source of phenol and acetone [1], cymene, from which it is possible to obtain styrene homologs (monomers for the preparation of synthetic rubber) [2], alkylphenols, used for detergents, phenol-formaldehyde resins and starting materials for preparing frost-resistant rubbers [3], halogen derivatives of benzene, which may be used as intermediates for various syntheses, especially for the preparation of halostyrenes [4] etc. The yield of alkylproducts reached 73% in the case of cumene, 79% for cymene, 81% for isopropylphenol, 69% for isopropylbromobenzene and 63% for isopropylchlorobenzene, calculated on the alcohol taken for the reaction. The alkylation of nitrobenzene did not give positive results.

Fig. 1. Dependence of isopropylphenol yields on operating time of catalyst (210°; 0.2 hours^{-1}; 6 : 1)

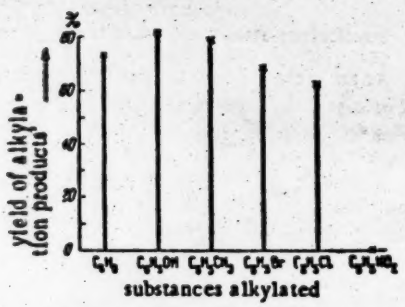


Fig. 2. Dependence of alkylation product yields on the substituents in the benzene ring.

In the work it was also shown that the activity of the catalyst remained quite high over a run of approximately 19 hours (Fig. 1).

The data obtained indicates that the use of aluminosilicate catalysts for alkylation (under our conditions) is advantageous, considering also the simplicity of their regeneration and their anticorrosive properties.

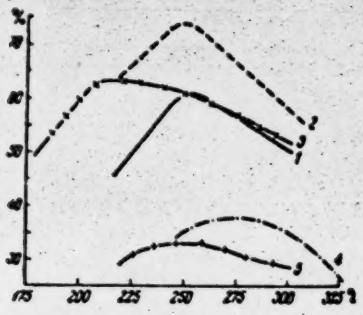


Fig. 3. Dependence of alkylation product yields on temperature (0.2 hours^{-1}; 6 : 1): 1) benzene, 2) toluene, 3) phenol, 4) bromobenzene, 5) chlorobenzene

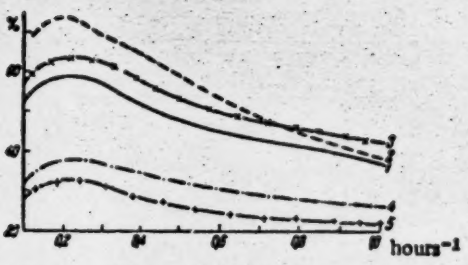


Fig. 4. Dependence of alkylation product yields on volume rate (optimal temperature; 6 : 1): 1) benzene, 2) toluene, 3) phenol, 4) bromobenzene, 5) chlorobenzene

TABLE 1

Molar ratio of reagents	Yields of alkylation products in percents									
	isopropyl-benzene		isopropyl-toluene		isopropyl-phenol		isopropylbro-mobenzene		isopropylchloro-benzene	
	I*	II**	I	II	I	II	I	II	I	II
2 : 1	29,6	29,8	39,0	40,8	39,0	—	16,5	19,5	13,0	14,5
4 : 1	53,0	58,6	60,0	62,6	58,0	58,7	31,0	37,0	31,0	33,0
6 : 1	59,0	64,6	74,0	80,2	63,5	73,9	38,0	45,0	33,0	39,5
8 : 1	60,2	68,5	74,8	82,5	70,0	—	42,0	53,5	40,0	50,5
20 : 1	73,5	94,0	79,5	96,3	81,0	98,0	69,0	92,0	63,3	81,0

* Pure starting materials

** The same substances, but unreacted in previous experiments (excess).

Insufficient attention is paid to the kinetics of alkylation in the presence of aluminosilicate catalysts.

As an approach to this problem, in the present work we investigated the effect of various factors on the yield of monoalkyl products, namely the effect of the nature of the functional groups in the benzene ring, the reaction temperature, the volume rate of reagent input and the molar ratio of the components.

The data we obtained agreed well with theoretical ideas based on the different activities of functional groups. The greater reactivity of phenol and toluene in electrophilic substitution as compared with benzene is explained by the capacity of 1st order orientants for strongly increasing the electron density of the nucleus.

The presence of m-cymene as well as p-cymene in the alkylation products of toluene contradicted data on the predominating orienting effect of the methyl group into the o- and p-positions. However, in the catalytic alkylation of benzene homologs, the main reaction product is usually the m-isomer [5]. According to literature data [6], the ratio of the products of normal and anomalous orientation depends on the alkylation conditions. The higher the activity of the catalyst, the longer the reaction and the higher the temperature, the greater is the tendency for the formation of the anomalous m-derivative.

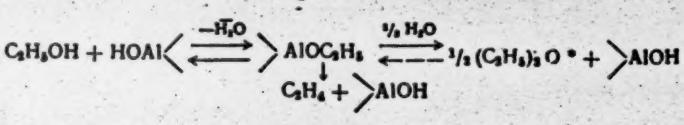
The somewhat lower yields of isopropylbromo- and isopropylchlorobenzenes in comparison with the yields of cumene are explained by the fact that, as is known, the distribution of electron density in the molecule of bromo- and especially chlorobenzene is such that an electrophilic substitution reaction is hindered in comparison with benzene.

The presence of a nitro group in the benzene nucleus decreases the electron density of the ring even more strongly, especially in the o- and p-positions. This fact agrees well with the data we obtained (Fig. 2).

The mechanism of catalytic alkylation of aromatic compounds by alcohols has not been explained conclusively. There is the opinion that the alkylation may proceed either by direct interaction of aromatic compounds with alcohols or with olefins or ethers obtained by preliminary dehydration of the alcohols.

To explain the mechanism of alkylation of aromatic compounds by alcohols in the presence of aluminosilicate catalysts, it is necessary to have in view the following: an aluminosilicate catalyst contains [7] three types of hydroxyl group, which differ in their positions. The acid hydrogen ion of a hydroxyl group of an aluminosilicate center acts as a catalyst for many reactions involving proton transfer. Alkylation is one of these reactions [8].

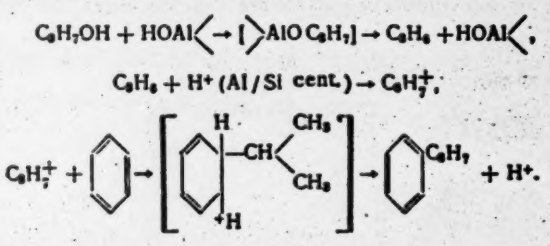
The dehydration of alcohols (for example ethyl alcohol) on an aluminosilicate surface proceeds by the following scheme [10]:



According to our observations, the dehydration of isopropyl alcohol to propylene on an aluminosilicate surface proceeds very readily (apparent activation energy of 6000 kcal/mole).

The propylene obtained forms a positively charged "carbonium ion" with the hydrogen of the hydroxyl group of an aluminosilicate center. Further interaction of the "carbonium ion" with a benzene nucleus leads to the formation of alkyl products and regeneration of the proton [12, 14, 15].

In a general form, the mechanism of the reaction we studied may be described by the following equations:



The alkylation was carried out in the presence of 100 ml of commercial aluminosilicate balls in a standard flow apparatus. The experiment duration was varied from 1 to 3.5 hours with the reacting components introduced at rates over the range from 0.1 to 1.0 hours^{-1}. The experimental temperature was varied from 200 to 350°.

The optimal yields of cumene, cymene and isopropylchlorobenzene were obtained at 250°, of isopropylbromobenzene at 275° and of isopropylphenol at 210 – 230° (Fig. 3). In all cases the volume rate reagent input was 0.2 hours^{-1} (Fig. 4). By studying the dependence of the monoalkyl product yields on the molar ratio of the reacting components, it was established that a decrease in the concentration of alcohol in the mixtures promoted an increase in the yields of monoalkyl products. This was especially sharply expressed on increasing the concentration of the substance alkylated from 2 to 6 molecules per molecule of alcohol. In this case the yield of alkyl products increased by a factor of two.

By the use of mixtures containing unreacted (in previous experiments) excess benzene, toluene, halobenzenes and phenols in a ratio of 20 molecules per molecule of alcohol the yield of monoalkyl products under optimal conditions was increased in certain cases from 73 to 94% (Table 1). We explain this increase in the yields by the presence in the reaction mixture of insignificant amounts of unsaturated compounds, activating the alkylation reaction [16].

• Diisopropyl ether was not formed under our conditions.

On the example of phenol alkylation it was established that during the first 5 hours of operation the activity of the catalyst was quite high (75% yield of alkylphenols), then it fell somewhat and became constant for a further 15 hours (60 – 65% yield of alkylphenols) and after this the activity fell sharply (Fig. 1). The activity of the catalyst was restored completely by the passage of a strong stream of dry air for 2 – 2.5 hours at 500 – 550°.

Individual alkylation products were isolated by distillation on columns with an efficiency of 40 and 80 t.p.

The structure of the alkylation products was confirmed by the preparation of derivatives and in some cases by spectral analysis.

The cumene obtained had constants corresponding to literature data: b.p. 151.5 – 151.7°/ 750 mm; n_D^{20} 1.4919; d_4^{20} 0.8624; cymene had b.p. 89°/ 45 mm; n_D^{20} 1.4931; d_4^{20} 0.8613. By spectral analysis it was established that the latter consisted of a mixture of approximately 63% of the p-isomer and 37% of the m-isomer.

Alkylation of chlorobenzene yielded o- and p-isopropylchlorobenzenes with the following constants: the o-isomer had b.p. 189-190.5°/ 760 mm; n_D^{20} 1.5170; d_4^{20} 1.0338; the p-isomer had b.p. 193 – 194.5°/ 760 mm; n_D^{20} 1.5130; d_4^{20} 1.0223. Oxidation of these yielded o-chlorobenzoic acid with m.p. 143° and p-chlorobenzoic acid with b.p. 241 – 242°.

Alkylation of bromobenzene yielded a mixture of o- and p-isopropylbromobenzenes with b.p. 212 – 212.7°/ / 753 mm; n_D^{20} 1.5371 and d_4^{20} 1.2840. Oxidation of this yielded o-bromobenzoic acid with m.p. 148.5° and p-bromobenzoic acid, m.p. 256°.

Alkylation of phenol yielded o-isopropylphenol with b.p. 124 – 124.3°/ 41 mm, m.p. 15.5°; n_D^{20} 1.5282; d_4^{20} 0.9963 and p-isopropylphenol with m.p. 51°. From them we obtained o- and p-isopropylphenoxyacetic acids with m.p. 131.5 and 81.5°.

Isopropyl phenyl ether was not detected among the reaction products.

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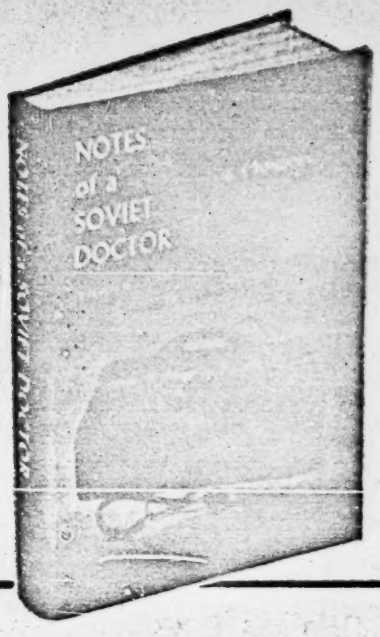

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